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PROCEEDINGS OF THE ROYAL SOCIETY.

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.

Speculations concerning the α -, β - and γ -Rays of Ra B, C, C'.— Part I. A Revised Theory of the Internal Absorption Coefficient.

By R. H. FOWLER, F.R.S.

(Received June 12, 1930.)

§ 1. *Introduction.*—It is well known that the γ -rays emitted by radioactive nuclei are often very strongly absorbed in a species of photoelectric effect by the planetary electrons of the parent atom, thus giving rise to the sharp *lines* of the β -ray spectrum. The recent work of Ellis and Aston provides numerical values of this "internal conversion coefficient" of the γ -rays from Ra BC and Ra CC'D†—data which bring out more clearly than hitherto the curiosities of this coefficient (see Table I below). The present paper is the outcome of

Table I.—Values of the Internal Conversion Coefficient in the K-Level for certain of the γ -rays of Radium B and Radium C.

$h\nu$ of the γ -ray in volts $\times 10^{-6}$.	Internal conversion coefficient.	$h\nu$ of the γ -ray in volts $\times 10^{-6}$.	Internal conversion- coefficient.
Radium B.		Radium C.	
2.43	0.25	9.41	0.0061
2.97	0.15	11.30	0.0062
3.54	0.10	12.48	0.0057
		13.90	0.0014
		14.26	> 0.07
6.12	0.0061	17.78	0.0016
7.73	0.0048	22.19	0.0013

† For general descriptive purposes it is convenient to speak of the γ -rays as arising from a radioactive transformation rather than to assign them to a particular nucleus. Hence the above notation.

repeated discussions between Dr. Ellis and the author about possible explanations of the data. All the preliminary work was carried out in collaboration, and it was our original intention to publish our results jointly. This has proved impossible, so that the responsibility for the corrections of the calculations of this paper rests entirely on me. But the work could not have been attempted without Dr. Ellis's help.

Ellis and Aston find that this coefficient behaves so differently for different classes of β -ray line that one is even sometimes tempted to suspect a different mechanism of emission. The rather soft γ -rays of Ra BC are converted by the K-level electrons in fractions of the surprising size of 10 per cent. to 25 per cent., varying in a normal manner with the frequency. The harder γ -rays of Ra CC'D fall, however, into three groups. The main γ -rays of energy from 6.12×10^5 to 12.48×10^5 volts have a practically constant conversion fraction of about 0.006; those from 13.90×10^5 to 22.19×10^5 volts a similar constant fraction now about 0.0015. All these γ -rays, though most easily studied via their derived natural β -ray lines undoubtedly can be studied as γ -rays outside their parent atom. But there is a third group containing one outstanding γ -ray of 14.26×10^5 volts energy whose existence has been inferred only from certain associated β -ray lines, among the strongest in the spectrum. This γ -ray (if it is a γ -ray) is so strongly converted in the parent atom that it is doubtful if it has ever been observed as a γ -ray at all. It would be consistent with (though not necessitated by) the evidence, to assert that it is a γ -ray with an internal conversion factor unity.†

The problem of the internal conversion of the γ -rays has been discussed theoretically by Miss Swirles in two papers.‡ She treats the nucleus as containing an oscillating Hertzian doublet of frequency ν which perturbs the surrounding planetary electrons and thereby induces photoelectric transitions to states of positive energy. The frequency of occurrence of these transitions can be exactly computed (on these assumptions) from the components of the interaction matrix for the field of the Hertzian doublet. The internal conversion fraction is then given by the ratio of the photoelectric transition frequency to the frequency of the radiative transitions in the nucleus resulting in the emission of a γ -ray. In the theory the rate of radiation of energy by

† The best evidence for its real existence as a γ -ray is provided by some experiments by Skobelzyn, 'Z. Physik,' vol. 58, p. 598 (1929). These suggest that it does exist, though abnormally rarely for the strength of its β -ray lines. Though we shall discuss the β -ray lines as if there were no corresponding γ -ray, we shall see that an abnormally infrequent corresponding γ -ray creates no difficulty for our theory.

‡ Swirles, 'Proc. Roy. Soc.,' A, vol. 116, p. 491 (1927) and vol. 121, p. 447 (1928).

the Hertzian doublet is taken to be classical and the frequency of its radiative transitions is therefore given by the classical rate divided by $h\nu$.

The problem can, of course, also be handled as a problem of the direct calculation of the rate of transitions in an atomic system between states of equal energy. The atomic system in zero approximation must now be thought of as a separate nuclear system and an external electronic system, without interaction except for the constant electrostatic field of the total nuclear charge, which are then coupled together by the electromagnetic forces arising from some oscillating structure in the nucleus itself. If we now make assumptions about this interaction which reduce it to a field of the nature of the electromagnetic field of a Hertzian doublet (with retarded potentials if necessary), the same results for the rate of ejection of β -rays are naturally obtained whether the process is regarded as one of direct interaction or of the emission and re-absorption of radiation. This also has been pointed out by Miss Swirles in her (unpublished) doctorate thesis. Miss Swirles's results in general disagree with experiment by giving a conversion coefficient for normal γ -rays about 10 times too small.

It was natural at first to hope that the internal conversion coefficient could really be treated in this way as an ordinary photoelectric absorption coefficient, modified only by the peculiar spatial relationship of the photon and the absorbing electron. It might still be possible to hold this view if it were a question of a fairly regular disagreement between calculation and experiment by a factor of the order of 10 or by a slightly different variation with the frequency of the γ -ray. Such discrepancies might conceivably be introduced by the use of hydrogen wave-functions. Ellis's and Aston's results forbid this view, if not in general, at least for the abnormal γ -ray at 14.26×10^5 volts. It seems legitimate therefore to attempt a revised attack by introducing explicitly some speculative nuclear structure and examining what extra interaction effects (if any) one can find between some quantum-mechanical nuclear system and the K- and other electrons of the outer atom. Dr. Ellis and the author cannot claim that they have thus achieved any general success, but they have been led to a new point of view and a new attempt to systematise the facts for Ra CC'D. The value of this general attempt is still very uncertain. However, one definite particular point emerges, which has been overlooked hitherto, but now enables one to interpret, in a satisfying way the queerest of all the γ -rays, the 14.26×10^5 volt ray of Ra CC'D.

§ 2. *Descriptive Statement of Results.*—We start by supposing that the nucleus contains some quantum-mechanical system carrying a charge, which

possesses a series of stationary states and is not necessarily initially found in its normal or ground state when γ -rays are about to be emitted as by the nucleus of Ra C' after the departure of the *nuclear* β -particle which creates Ra C' out of Ra C. The external atomic system is thought of for simplicity as containing a single electron in the Coulomb field of a charge $+Ze$. This electron is initially in its ground level being usually a K-ring electron. This is the complete system to zero order approximation. To the next approximation there is, however, a non-stationary interaction between the nuclear system and the electron of potential energy Qe^2/R , where R is the distance between the electron and the nuclear system. To obtain exact results directly comparable with those of Miss Swirles we must replace $1/R$ by the corresponding retarded potential and include also electromagnetic forces due to the "currents" in the oscillatory nuclear system. These refinements, however, we shall omit to avoid complications which can hardly affect the "order of magnitude" type of discussion which is all that we can legitimately aim at. Of this interaction a part Qe^2/r_e is really stationary and has already been allowed for in the Coulomb field of the nucleus. Here r_e denotes the distance of the electron from the centre of the nucleus and with an obvious notation

$$R = |\mathbf{r}_e - \mathbf{r}_n|. \quad (1)$$

Thus the simplified interaction which couples the nuclear system and the electron is

$$Qe^2 \left\{ \frac{1}{R} - \frac{1}{r_e} \right\}. \quad (2)$$

This interaction can, of course, in the well-known way, induce transitions to other states of equal energy of the combined system nucleus and external electron. These include the state in which a γ -ray has left the combined system—this process we may call a radiative transition of the combined system—and also states in which the excited nucleus has fallen to a lower energy level and the bound K-electron has become a free electron of positive energy E' . This is always possible for the E' states form a continuum. The value of E' is given by

$$W - E = W' + E', \quad (3)$$

where W , W' are the nuclear energy levels referred to some convenient zero. This can also be written

$$E' = W - W' - E = h\nu - E, \quad (4)$$

where ν is the frequency of the γ -ray which might emerge and be observed externally in the radiative alternative of the process. This process we may call an external β -ray transition of the combined system, but the adjective *external* may be omitted when there is no danger of confusion with a primary β -ray change in the nucleus.

We shall be primarily concerned with transitions of this latter type. Their frequency of occurrence can be calculated by the method of variation of parameters,[†] and is found, as is well known, to depend on the square of the modulus of the integral b ,

$$b = Qe^2 \iiint (\psi_n \psi_e)_1 \left\{ \frac{1}{R} - \frac{1}{r_e} \right\} (\psi_n \psi_e)_2^* d\omega_n d\omega_e, \quad (5)$$

taken over the six-dimensional configuration space of the combined system. The ψ 's represent respectively the normalised wave-functions of the initial and final states of the nuclear system and electron in zero order approximation without their time factors.

When we come to evaluate this integral we find that Miss Swirles's treatment is equivalent to assuming that $r_e > r_n$ in every region which makes a sensible contribution to b . This is equivalent to assuming that the effective spatial extension of the nuclear wave-functions in their own co-ordinate space is indefinitely small or, if the reader prefers, that "the nucleus is indefinitely small." On looking further into this approximation we find that it is not justified. The most striking failure is where in Miss Swirles's approximation $b = 0$ whereas when the region $r_n > r_e$ is included $b \neq 0$. This corresponds to the case in which the pair of nuclear states has no dipole moment, and therefore, at least to a first approximation, cannot radiate a γ -ray. In Miss Swirles's approximation no transition can then happen, not even β -ray transitions of the combined system. But actually $b \neq 0$, β -ray transitions can occur, although (by the nuclear selection rules) the corresponding γ -ray can never be emitted. The relative frequency of such events depends of course on the size of the nucleus. Though in parallel cases these extra β -ray transitions are usually theoretically considerably less frequent than the ordinary ones associated with γ -rays, it seems that they may be important in the interpretation of the spectrum.

The strong abnormally converted β -ray at 14.26×10^5 volts at once springs to mind. We suggest that *this results from an excited nuclear state from which*

[†] This has been conveniently and compactly expounded recently by Born, 'Z. Physik,' vol. 58, p. 306 (1929). See also Dirac, 'Proc. Roy. Soc.,' A, vol. 112, p. 661 (1926). We use Born's arrangement here, modified to correct for minor oversights.

a radiative transition is impossible. Nor is this all, for, as has been often pointed out† before, the energy difference 14.26×10^6 volts lies strikingly close to the difference of energy between the normal 7 cm. α -particles and the longer range group of 9.2 cm. Exact comparison is difficult as the energy of the 9.2 cm. group has not been directly measured by a deflection method. I am informed by Sir E. Rutherford that the most reliable estimate of their energy is to be obtained as follows:—The α -particles from Th C' have an extrapolated range 8.61 cm. and an energy 8.764×10^6 volts. Extrapolation to a range of 9.25 cm. (the extrapolated range for the 9.2 cm. group of Ra C' estimated by Feather and Nimmo‡) should probably be made for ranges in this region by use of the law

$$R \propto V^{3.2}.$$

This yields an energy of 9.158×10^6 volts. The energy of the 7 cm. α -particle + 1.426×10^6 volts is $(7.683 + 1.426)10^6 = 9.109 \times 10^6$ volts, disagreeing by 5 parts in 900. Exact agreement would result if the 3.3 power were to be replaced by a 3.8 power, or the range 9.25 cm. by 9.16 cm. No such change is justified by existing knowledge, but the agreement as it is is still quite striking enough. Suppose then that the lower nuclear level in this transition is the normal state of the Ra C' nucleus, and the nuclear system the α -particle which leaks out according to the Gamow-Gurney-Condon theory with a mean life of about 10^{-5} seconds. The upper state will then possess a still greater rate of α -particle leak, but will in addition have open to it the chance of an external β -ray transition to the normal state of slower leak. The relative frequency of these two events will depend on the ratio of the lives of the upper state as against two alternative processes. The 14.26×10^6 volt β -ray is observed to be emitted 25 times per 10,000 disintegrations, the 9.2 cm. α -particle 28 times per million,§ say one 9.2 cm. α -particle to every 100 of these β -rays. The life of the upper state against α -particle leak has been estimated for me by Dr. Gamow at about 4×10^{-9} second. The main uncertainty lies in the assumed life of the normal Ra C' nucleus. The life of the upper state against external β -ray emission can be 2.5×10^{-11} second on most natural assumptions about the nuclear system. It seems to us fairly conclusive that *this abnormal β -ray has thus been properly accounted for as a side product of the purely α -ray*

† E.g., Feather, 'Phys. Rev.', vol. 34, p. 1558 (1929).

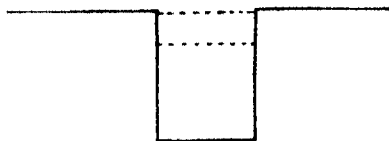
‡ Feather and Nimmo, 'Proc. Roy. Soc., A', vol. 122, p. 668 (1929).

§ For the β -ray, Ellis and Aston, 'Proc. Roy. Soc., A' (*infra*, p. 180). For the α -particle, Rutherford, 'Phil. Mag.', vol. 37, p. 537 (1919) and Rutherford and Chadwick, 'Phil. Mag.', vol. 48, p. 509 (1924).

disintegration of the special type yielding 9.2 cm. particles, no radiative process of any type being concerned.

Let us now return to the other γ -rays, all of which are "converted" into β -rays to a much more normal degree. If the observed dependence on frequency were more nearly normal one might say that all of them were converted about 10 times more often than the straightforward emission and absorption theory would lead one to expect. We have therefore been led to examine whether any natural assumptions can be made which will increase the contribution to the integral for b from those regions $r_n > r_e$ where Miss Swirles's approximations are inadequate. We first made a thorough examination of a nucleus in which the potential energy of the α -particle (or other oscillating system) has the form of a spherically symmetrical box with infinitely high walls. It appears that the errors in Miss Swirles's theory could not be serious for any box of a size permissible from other knowledge of nuclear structure except for the complete omission of certain transitions which we have noted above.

We then examined a nucleus with a potential of box form with walls of finite height, in order to see if the spread of the nuclear wave-functions beyond the box walls could be enough to influence the calculations. It appears again that, if the oscillating nuclear system is of a mass comparable with that of an α -particle, though the spread of the wave-function of the upper nuclear state could be great enough to endanger Miss Swirles's approximation, that of the lower nuclear state cannot be large, and, as it is always the product of the wave-functions of the two states which is concerned, Miss Swirles's approximation should hold. This can be made clearer with a diagram.



The rectangular curve represents the radial distribution of the potential energy of the oscillating system, the cross lines in the box the energies of two of its stationary states. The upper level can be so high that the spread of the wave-function beyond the walls can be extensive, even if the total energy of the particle is less than that of rest at infinite separation so that it can never leak out. But if the particle is to lose some of its oscillatory energy and fall to the lower level, this step is of the order of half a million volts, and the level will be so far below the top of the walls that the spread of the wave-function must be

extremely restricted. There seems no prospect therefore of the large conversion factors being provided by such a model.

This failure does not extend, however, to a model in which the nucleus contains an oscillating system, say, an α' - or α'' -particle† which itself contains extra internal energy, capable of transfer by radiation or collision. Such a system, oscillating in the main nucleus in the top level of fig. 1, will be capable of frequent interactions with a K-electron provided that only its internal state is concerned and not its main oscillations. There seems no reason why such a system might not exhibit any ratio whatever between the frequencies of β -particle ejection and γ -ray emission. Exact calculations have not yet been made but the actual qualitative possibilities have led Dr. Ellis and myself to the speculative systematisation of Ra BCC'D already mentioned. We are, however, still too uncertain of its value to say more about it here, and intend shortly to attempt some more precise calculations.

§ 3. *Details of an "Experimental" Nucleus.*‡ As we have explained we require details of the wave-functions for a quantum-mechanical system of charge Qe confined to a spherical box by a potential energy which we shall take for simplicity as

$$V = 0 \quad (r < a) \quad V = C \quad (r > a). \quad (6)$$

In the simplest applications we shall put $C = \infty$. The complete wave-equation, apart from relativistic modifications, is

$$-\frac{\hbar^2}{8\pi^2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \\ + V + \frac{\hbar}{2\pi i} \frac{\partial}{\partial t} \} \Psi = 0. \quad (7)$$

Put

$$\Psi = e^{-\frac{2\pi i}{\hbar} W t} \psi, \quad \psi = \frac{1}{r} Y_l^m \chi(r), \quad (8)$$

where Y_l^m is a standard spherical harmonic, one of the set

$$(1 - \mu^2)^{\frac{1}{2}m} \left(\frac{\partial}{\partial \mu} \right)^m P_n(\mu) e^{\pm im\phi} \quad (m = 0, 1, \dots, l),$$

suitably normalised by a rule given later. Then

$$\frac{d^2 \chi}{dr^2} + \left\{ \kappa^2 (W - V) - \frac{l(l+1)}{r^2} \right\} \chi = 0. \quad (9)$$

† Names sometimes given to hypothetical structures composed of one α -particle plus one or two extra electrons respectively all compressed to α -particle dimensions.

‡ In this section where only the nucleus is discussed we shall omit the distinctive suffix n .

Since l is an integer (or zero) and V is constant this equation is equivalent to Bessel's equation of half odd integral order, so that the solutions for all values of l are always elementary functions. Bessel's equation of order $l + \frac{1}{2}$, modified so that the solutions are $0 = z^{\frac{1}{2}} J_{\frac{1}{2}(l+1)}(z)$, is

$$\theta'' + \left\{ 1 - \frac{l(l+1)}{z^2} \right\} \theta = 0. \quad (10)$$

To handle any values of l and C is therefore merely a matter of algebra. As we shall only use in the discussion the particular cases $C = \infty$ and $l = 0$ we confine attention to these.

Case (i). $C = \infty$. We have to solve

$$\frac{d^2\chi}{dr^2} + \left\{ \kappa^2 W - \frac{l(l+1)}{r^2} \right\} \chi = 0, \quad (11)$$

subject to $\chi(0) = 0$, $\chi(a) = 0$.† For values of $r > a$, $\chi \equiv 0$. By comparison of (10) and (11) we see at once that

$$\chi = (\kappa r \sqrt{W})^{\frac{1}{2}} J_{l+\frac{1}{2}}(\kappa r \sqrt{W}), \quad (12)$$

and the characteristic values of the energy are determined by the equation

$$\kappa a \sqrt{W} = \alpha_n, \quad (13)$$

where α_n is the n th positive root of the equation

$$J_{l+\frac{1}{2}}(x) = 0. \quad (14)$$

[One may record here a general property of the roots of Bessel's equation which leads to an arrangement of the various energies presumably true also of similar equations. It is that the roots of $J_{l+\frac{1}{2}}(x)$ separate the roots of $J_{l+\frac{3}{2}}(x)$ the least positive root of $J_{l+\frac{3}{2}}(x)$ being greater than the least positive root of $J_{l+\frac{1}{2}}(x)$. In symbols

$$\alpha_{n,l} < \alpha_{n,l+1} < \alpha_{n+1,l}. \quad (15)$$

The second of these inequalities specifies the relative order of the energy values belonging to a given total quantum number $n + l + 1$. *Energy values of the same total quantum number decrease with increasing l .*]

† It is always assumed that χ must vanish at $r = 0$ to make $\psi(r)$ finite there. But the commonly used more general condition, that $\int_0^a |\psi|^2 dr$ must converge as $r \rightarrow 0$, allows $\chi(r)$ to be *bounded*, and for $l = 0$ does not select one solution. The condition $\chi(0) = 0$ seems clearly correct and necessary, but does not follow from the generally accepted postulate. The difficulty perhaps disappears in a relativistic version.

We have now constructed a wave-function

$$\psi = \frac{A}{r} Y_l^m (\kappa r W)^{\frac{1}{2}} J_{l+\frac{1}{2}} (\kappa r \sqrt{W}), \quad (16)$$

in which W is determined by (13) and (14). If we assume that the Y_l^m are so normalised that

$$\iint (Y_l^m)^2 \sin \theta d\theta d\phi = 4\pi,$$

the A 's must be determined so that

$$4\pi A^2 \kappa \sqrt{W} \int_0^a r J_{l+\frac{1}{2}}^2 (\kappa r \sqrt{W}) dr = 1,$$

or since†

$$\int_0^a r J_{l+\frac{1}{2}}^2 (\kappa r \sqrt{W}) dr = \frac{1}{2} a^2 J_{l+\frac{1}{2}}'^2 (\kappa a \sqrt{W}),$$

$$A^2 = \frac{1}{2\pi a^2 \kappa \sqrt{W} J_{l+\frac{1}{2}}'^2 (\kappa a \sqrt{W})}. \quad (17)$$

When $\kappa a \sqrt{W} = \alpha_n$ the corresponding value of the normalising A will sometimes be written $A_{l,n}$.

Case (ii). C finite, $l = 0$. We have to solve

$$\frac{d^2 \chi}{dr^2} + \kappa^2 W \chi = 0 \quad (r < a), \quad (18)$$

$$\frac{d^2 \chi}{dr^2} - \kappa^2 (C - W) \chi = 0 \quad (r > a). \quad (19)$$

The solutions must be of the form

$$\chi = A \sin (\kappa r \sqrt{W}) \quad (r < a),$$

$$\chi = B e^{-\kappa(r-a) \sqrt{C-W}} \quad (r > a),$$

both χ and $d\chi/dr$ being continuous at $r = a$. This requires

$$A \sin (\kappa a \sqrt{W}) = B,$$

$$A \sqrt{W} \cos (\kappa a \sqrt{W}) = -B \sqrt{C - W}.$$

The characteristic energies are the roots of the equation

$$\tan (\kappa a \sqrt{W}) = - \sqrt{\frac{W}{C - W}} \quad (20)$$

† For example, Gray and Matthews, 'Bessel's Functions,' p. 53.

or

$$\kappa a \sqrt{W} = s\pi - \arctan \sqrt{\frac{W}{C-W}} \quad (s = 1, 2, 3, \dots), \dagger \quad (20')$$

and

$$B = (-)^{s-1} A \sqrt{\frac{W}{C}}. \quad (21)$$

The complete wave-function may now be written

$$\psi = \frac{A}{r} \sin(\kappa r \sqrt{W}) \quad (r < a) \quad (22)$$

$$\psi = (-)^{s-1} \sqrt{\left(\frac{W}{C}\right)} \frac{A}{r} e^{-\kappa(r-a) \sqrt{(C-W)}} \quad (r > a). \quad (23)$$

Normalisation is effected by making

$$4\pi \int_0^\infty |\psi|^2 r^2 dr = 1,$$

which easily reduces to

$$A^2 = \frac{1}{2\pi \{a + 1/\kappa \sqrt{(C-W)}\}}. \quad (24)$$

§ 4. *General Theory of the Interaction of the Nucleus and one External Electron.*—In zero order approximation we can write the wave-functions of the combined system including their time factors in the form†

$$\Psi = (\Psi_n \Psi_e)_1, (\Psi_n \Psi_e)_2, \dots,$$

all being solutions of the separable wave-equation

$$\left[H_n + H_e + \frac{h}{2\pi i} \frac{\partial}{\partial t} \right] \Psi = 0. \quad (25)$$

By the usual variation of parameters we attempt to solve the more exact equation

$$\left[H_n + H_e + Qe^2 \left\{ \frac{1}{R} - \frac{1}{r_e} \right\} + \frac{h}{2\pi i} \frac{\partial}{\partial t} \right] \Psi = 0,$$

by an expression of the form

$$\Psi = \sum_p a_p(t) (\Psi_n \Psi_e)_p,$$

† There is no possible root for $s = 0$ and the series of roots continues until a value of s is reached for which $W > C$.

‡ Of course, if the oscillating nuclear system is an electron, these expressions would have to be modified to allow for the *exchange degeneracy*. In Born's method (until the final limiting process) all the electronic wave-functions form a *discrete set*.

which leads to

$$\frac{\hbar}{2\pi i} \Sigma_p \dot{a}_p(t) (\Psi_n \Psi_e)_p + Q\varepsilon^2 \left(\frac{1}{R} - \frac{1}{r_e} \right) \Sigma_p a_p(t) (\Psi_n \Psi_e)_p = 0.$$

Here we suppose that the initial state of the system has suffix 1, so that $a_1(0) = 1$, $a_p(0) = 0$, $p \neq 1$. We then find by the usual argument, using normalised wave functions, that approximately

$$-\frac{\hbar}{2\pi i} \dot{a}_q = \iint (\Psi_n \Psi_e)_q^* Q\varepsilon^2 \left(\frac{1}{R} - \frac{1}{r_e} \right) (\Psi_n \Psi_e)_1 d\omega_n d\omega_e, \quad (26)$$

the integrations being over the six-dimensional configuration space. From this it follows by Born's argument that if $W(t)$ is the probability of a transition during a comparatively long time t to a state in which the nuclear wave-function has the suffix s and the electron is free, with positive energy E' given by (4), then

$$\frac{W(t)}{t} = \frac{4\pi^2}{\hbar} \frac{d\lambda(E')}{dE'} |b_q|^2_{E_q \rightarrow E'}. \quad (27)$$

In this equation $\lambda(E')$ is the limiting functional form of the relationship, $q = \lambda(E_q)$, between the integer q enumerating the electronic states of positive energy when they are originally confined artificially to a sphere of radius D and $D \rightarrow \infty$. The relevant component of the interaction matrix, b_q , is given by

$$b_q = Q\varepsilon^2 \int (\psi_e)_q^* (\psi_e)_1 d\omega_e \int (\psi_n)_s^* (\psi_n)_1 \left\{ \frac{1}{R} - \frac{1}{r_e} \right\} d\omega_n; \quad (28)$$

the omission of the time factors from the ψ 's is indicated by the use of small letters. Since any two of the nuclear wave-functions are orthogonal the term in $1/r_e$ may be omitted.

In (28)

$$R^2 = r_e^2 + r_n^2 - 2r_e r_n \cos \Theta,$$

where

$$\cos \Theta = \cos \theta_e \cos \theta_n + \sin \theta_e \sin \theta_n \cos (\phi_e - \phi_n).$$

When $r_n < r_e$

$$\frac{1}{R} = \frac{1}{r_e} + \Sigma_t \frac{(r_n)^t}{r_e^{t+1}} P_t(\cos \Theta), \quad (29)$$

with a similar expression when $r_n > r_e$.

Let us now suppose that the nuclear wave-functions are of the general type studied in § 3, namely, wave-functions for a spherically symmetrical field, so that the co-ordinates θ_n , ϕ_n appear only in a separate spherical harmonic

factor Y_l^m . Then in the θ_n, ϕ_n integrations we are concerned always with factors of the type.

$$\iint P_l(\cos \Theta) Y_l^m [Y_l^m]^* \sin \theta_n d\theta_n d\phi_n.$$

It will lead us to unnecessary complication for the purpose in hand to consider the general case. We shall therefore confine attention to cases in which one l is zero—for definiteness this will be taken to be $l_s = 0$, so that $[Y_l^m]^* \equiv 1$. We then find, by the well-known rule,

$$\begin{aligned} \iint P_l(\cos \Theta) Y_l^m \sin \theta_n d\theta_n d\phi_n &= \frac{4\pi}{2l_1 + 1} Y_l^m(\theta_e, \phi_e) \quad (l = l_1), \\ &= 0 \quad (l \neq l_1). \end{aligned}$$

Thus the inner integral in b_q reduces to an expression of the form

$$\frac{4\pi}{2l_1 + 1} \left\{ \frac{1}{r_e^{l_1 + 1}} \int_0^{r_e} \chi_s(r_n) \chi_l(r_n) r_n^{l_1} dr_n + r_e^{l_1} \int_{r_e}^{\infty} \chi_s(r_n) \chi_l(r_n) \frac{dr_n}{r_n^{l_1 + 1}} \right\} Y_l^m(\theta_e, \phi_e),$$

which can be written for shortness

$$\frac{4\pi}{2l_1 + 1} X(r_e) Y_l^m(\theta_e, \phi_e).$$

We now introduce the electronic wave-functions. These have their usual form. If we confine attention to the more important effects which occur in the K- and L_I-electron groups we can take

$$\begin{aligned} (\psi_e)_1 &= \tau_1(r_e), \\ (\psi_e)_q^* &= [Y_l^m(\theta_e, \phi_e)]^* \tau_q^*(r_e), \end{aligned}$$

the τ 's being the radial factors. Their exact form is not required for the moment. Then

$$\begin{aligned} b_q &= \frac{4\pi}{2l_1 + 1} Q e^2 \int_0^{\infty} X(r_e) \tau_1(r_e) \tau_q^*(r_e) r_e^2 dr_e \\ &\quad \times \iint [Y_l^m(\theta_e, \phi_e)]^* Y_l^m(\theta_e, \phi_e) \sin \theta_e d\theta_e d\phi_e. \end{aligned}$$

This vanishes unless

$$Y_l^m = Y_{l_1}^{m_1}, \quad (30)$$

and then reduces to

$$b_q = \frac{16\pi^2}{2l_1 + 1} Q e^2 \int_0^{\infty} X(r_e) \tau_1(r_e) \tau_q^*(r_e) r_e^2 dr_e, \quad (31)$$

or in full

$$b_q = \frac{16\pi^2}{2l_1 + 1} Q z^2 \int_0^\infty \tau_1(r_e) \tau_q^*(r_e) \left\{ \frac{1}{r_e^{l_1-1}} \int_0^{r_e} \chi_s(r_n) \chi_1(r_n) r_n^{l_1} dr_n \right. \\ \left. + r_e^{l_1+2} \int_{r_e}^\infty \chi_s(r_n) \chi_1(r_n) \frac{dr_n}{r_n^{l_1+1}} \right\} \quad (32)$$

Equation (30) gives us the obvious selection rules necessary for the conservation of angular momentum. The transition to which (32) refers is one in which the nuclear radial and azimuthal numbers change $(n_1, l_1) \rightarrow (n_s, 0)$ and the electronic quantum numbers $(n_1', 0) \rightarrow (\text{free}, l_1)$. This is sufficiently general for our purposes. We shall in fact only discuss in detail $n_1' = 1$.

We can now see the effect of the usual approximations. If we assume that the nucleus is so "small" that we can neglect all contributions for which $r_n > r_e$, the second term in (32) vanishes and the first term can be taken over the range $0, \infty$. This important factor is then

$$\frac{1}{r_e^{l_1-1}} \int_0^\infty \chi_s(r_n) \chi_1(r_n) r_n^{l_1} dr_n.$$

When $l_1 = 0$ this vanishes by the orthogonality of the radial wave-functions, whereas the exact (32) does not. When $l_1 = 1$ it reduces to the usual factor in the dipole moment which enters similarly into this interaction and the usual formula for the rate of radiation. When $l_1 \geq 2$ it does not vanish but gives electric moments of higher order. These terms, however, will be found to be of smaller order. It is, however, not possible to make much further progress without introducing approximations based on particular nuclear wave-functions, and the properties of the actual electronic ones.

§ 5. *The Electronic Wave Functions*.—These are well known, but we shall take the opportunity of introducing the Barnes-Mellin integral representations of the wave-functions of positive energy, which are considerably simpler than the double circuit integrals usually used by writers on quantum mechanics. Sufficient references will be found in Whittaker and Watson's "Modern Analysis," and we shall, to avoid confusion, use their notation so far as possible, though it is not an ideal one.

The normalised wave-function for a K-electron of an atom of atomic number Z is

$$(\psi_e)_1 = \tau_1(r_e) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^3 e^{-Zr_e/a_0}, \quad (33)$$

where a_0 is the radius of Bohn's smallest hydrogen orbit.

The radial factor $\tau(r_e)$ in $(\psi_e)_e$ is that solution of the wave-equation

$$\frac{1}{r_e^2} \frac{d}{dr_e} \left(r_e^2 \frac{d\tau}{dr_e} \right) + \left\{ \kappa^2 \left(\frac{Z\varepsilon^2}{r_e} + E' \right) - \frac{l(l+1)}{r_e^2} \right\} \tau = 0 \quad \left(\kappa^2 = \frac{8\pi^2 m_e}{h^2} \right),$$

which is regular near $r_e = 0$, originally normalised for a sphere of large radius D ; m_e is the mass of the electron. On putting

$$\rho = 2i\kappa r_e \sqrt{E'} = i\alpha r_e, \quad (34)$$

$$k = -i\kappa Z\varepsilon^2 / (2\sqrt{E'}) = -i\beta, \quad (35)$$

we find that $\tau(r_e)$ is of the form $W(\rho)/r_e$, where $W(\rho)$ satisfies Whittaker's equation

$$\frac{d^2 W}{d\rho^2} + \left\{ -\frac{1}{4} + \frac{k}{\rho} - \frac{l(l+1)}{\rho^2} \right\} W = 0.$$

This equation is, of course, satisfied by hypergeometric functions of type ${}_1F_1$.

In the Barnes-Mellin representation and the notation of Whittaker and Watson, a pair of standard solutions of the equation are

$$W_{k, l+1}(\rho) = \frac{e^{-1/2\rho} \rho^k}{2\pi i} \int_{-\infty i}^{+\infty i} \frac{\Gamma(s) \Gamma(-s-k-l) \Gamma(-s-k+l+1)}{\Gamma(-k-l) \Gamma(-k+l+1)} \rho^s ds$$

$$(|\arg \rho| < \frac{3}{2}\pi), \quad (36)$$

$$W_{-k, l+1}(e^{-\pi i} \rho) = \frac{e^{-1/2\rho} e^{\pi i k} \rho^{-k}}{2\pi i} \int_{-\infty i}^{+\infty i} \frac{\Gamma(s) \Gamma(-s+k-l) \Gamma(-s+k+l+1)}{\Gamma(k-l) \Gamma(k+l+1)} e^{-\pi i s} \rho^s ds$$

$$(|\arg \rho - \pi i| < \frac{3}{2}\pi), \quad (37)$$

The contours are any contours parallel to the imaginary axis of s modified if necessary so as to leave all the poles of $\Gamma(s)$ to the left and all the other poles to the right. The asymptotic expansions for large ρ are obtained at once by shifting the contour towards the left over the poles of $\Gamma(s)$. It is easily proved by standard methods that

$$\frac{(-)^{l+1} W_{k, l+1}(\rho)}{\Gamma(1+l+k)} + \frac{W_{-k, l+1}(e^{-\pi i} \rho)}{\Gamma(1+l-k)}$$

$$= \frac{e^{1/2\rho}}{2\pi i} \frac{e^{\pi i k}}{\Gamma(1+l+k)} \int_{-\infty i}^{+\infty i} \frac{\Gamma(s+k) \Gamma(-s+l+1)}{\Gamma(1+s+l)} \rho^s ds$$

$$(|\arg \rho| < \frac{1}{2}\pi), \quad (38)$$

the contour separating the poles of $\Gamma(s+k)$ and $\Gamma(-s+l+1)$. By bending round the contour to enclose the poles of $\Gamma(-s+l+1)$ along the positive axis it is seen at once that this function can be represented by a power series

convergent for all ρ starting at ρ^{l+1} so that it is the solution regular near $\rho = 0$ which we require. By a more refined discussion of the asymptotic values of the Γ -functions we can show that if the contour $\frac{1}{2} - \infty i \rightarrow \frac{1}{2} + \infty i$ is used, which separates the poles for $l = 0, 1, \dots$, and purely imaginary k , the integral can be used for the range $|\arg \rho| \leq \frac{1}{2}\pi$, and therefore for the purely imaginary ρ of our wave-function. Putting in the values of k and ρ from (34) and (35), we therefore find that we may write

$$\tau(r_e) = \frac{A}{r_e} \frac{e^{\pi\beta + \frac{1}{2}iar_e}}{2\pi i \Gamma(1+l-i\beta)} \int_{\frac{1}{2}-\infty i}^{\frac{1}{2}+\infty i} \frac{\Gamma(s-i\beta) \Gamma(-s+l+1)}{\Gamma(1+s+l)} (ixr_e)^s ds. \quad (39)$$

For large r_e we find from (36) and (37) that

$$W_{k, l+\frac{1}{2}}(\rho) \sim e^{-\frac{1}{2}k} \rho^k, \quad W_{-k, l+\frac{1}{2}}(e^{-\pi i} \rho) \sim e^{\frac{1}{2}k} e^{\pi i k} \rho^{-k}. \quad (40)$$

It follows at once from (38) that

$$\begin{aligned} \tau(r_e) &\sim \frac{A}{r_e} \left\{ \frac{(-)^{l+1}}{\Gamma(1+l-i\beta)} e^{-\frac{1}{2}iar_e} (xr_e)^{-i\beta} e^{\frac{1}{2}\pi\beta} \right. \\ &\quad \left. + \frac{1}{\Gamma(1+l+i\beta)} e^{\frac{1}{2}iar_e} (xr_e)^{i\beta} e^{\frac{1}{2}\pi\beta} \right\} \\ &= \frac{2A}{r_e} \left| \frac{e^{\frac{1}{2}\pi\beta}}{\Gamma(1+l-i\beta)} \right| \cos \left\{ \frac{1}{2} \alpha r_e + \beta \log \alpha r_e + \mu \right\}, \end{aligned} \quad (41)$$

where μ is a constant. This $\tau(r_e)$ is to be so normalised that

$$4\pi \int_0^D |\tau(r_e)|^2 r_e^2 dr_e = 1,$$

so that

$$\frac{16\pi A^2 e^{\pi\beta}}{|\Gamma(1+l+i\beta)|^2} \int_0^D \cos^2 \left(\frac{1}{2} \alpha r_e \right) dr_e = 1,$$

from which it follows that

$$|A| = \frac{|\Gamma(1+l+i\beta)| e^{-\frac{1}{2}\pi\beta}}{\sqrt{(8\pi D)}}.$$

Thus the properly normalised $\tau(r_e)$ may be taken to be

$$\tau(r_e) = \frac{e^{\frac{1}{2}\pi\beta}}{\sqrt{(8\pi D)}} \frac{1}{r_e} \frac{e^{\frac{1}{2}iar_e}}{2\pi i} \int_{\frac{1}{2}-\infty i}^{\frac{1}{2}+\infty i} \frac{\Gamma(s-i\beta) \Gamma(-s+l+1)}{\Gamma(1+s+l)} (ixr_e)^s ds. \quad (42)$$

At this stage we can conveniently find the value of $d\lambda(E')/dE'$ required in (27). From the asymptotic form of $\tau(r_e)$ we see that if it is required to confine the wave-function to the sphere $r_e = D$ we must have

$$\frac{1}{2}\alpha D \sim \frac{1}{2}(2q+1)\pi \sim q\pi,$$

so that as $\alpha = 2\kappa\sqrt{E'}$, $g \sim \kappa D \sqrt{E'}/\pi$. This leads at once to the required relation

$$\lambda(E') \sim \frac{\kappa D \sqrt{E'}}{\pi}, \quad \frac{d\lambda(E')}{dE'} \sim \frac{\kappa D}{2\pi\sqrt{E'}}. \quad (43)$$

From (27) and (43) we now deduce that

$$\frac{W(t)}{t} = \frac{4\pi^2}{h^2} \sqrt{\frac{2m_e}{E'}} D |b_a|^2, \quad (44)$$

b_a being given by (32).

§ 6. *Numerical Values.*—Numerical values for certain of the constants entering the foregoing formulæ are required before methods of approximation can be adopted. We have for the electron

$$\kappa_e^2 = \frac{8\pi^2 m_e}{h^2} = 1.664 \times 10^{27}, \quad \kappa_e = 4.08 \times 10^{13}.$$

$$\sqrt{E'} = 1.261 \times 10^{-6} \sqrt{V}, \quad V \text{ in electron-volts.}$$

$$\alpha = 2\kappa_e \sqrt{E'} = 1.03 \times 10^8 \sqrt{V} \text{ cm.}^{-1}.$$

$$\beta = \kappa_e Z e^2 / (2\sqrt{E'}) = 3.09 \times 10^3 V^{-\frac{1}{2}} \quad (Z = 84).$$

$$a_0 = 5.28 \times 10^{-9} \text{ cm.}$$

For the radius of the nucleus we shall take

$$a = 2 \times 10^{-12} \text{ cm.}$$

Further, for an α -particle as nuclear oscillator

$$\kappa_n = 3.5 \times 10^{15}.$$

The value of a leads to

$$\alpha a = 2 \times 10^{-4} \sqrt{V}.$$

For a 10^6 -volt electron $\alpha a = 0.2$. This value of αa shows that it is proper to regard r_e as small in $\tau_e^*(r_e)$ when $r_e < a$, i.e., inside the nucleus. *A fortiori* r_e is small inside the nucleus for $\tau_1(r_e)$. The energy steps between the levels of our nucleus are such that

$$\Delta W_n = 5.11 \times 10^5 \frac{\Delta(s^2)}{(10^{12} a)^2} \text{ volts.}$$

§ 7. *The Evaluation of the Interaction Integral* (32) *when* $C = \infty$ *and the Transition in* l *is* $0 \rightarrow 0$.—In this particular case $l_1 = 0$ and the nuclear wave-functions $\chi(r_n)$ are all zero when $r_n > a$. We have

$$b_e = 16\pi^2 Q e^2 \int_0^\infty \tau_1(r_e) \tau_e^*(r_e) dr_e \left\{ r_e \int_0^{r_e} \chi_s(r_n) \chi_1(r_n) dr_n + r_e^2 \int_{r_e}^a \chi_s(r_n) \chi_1(r_n) \frac{dr_n}{r_n} \right\}$$

This form is only necessary when $r_e < a$. When $r_e > a$ the factor $\{ \}$ reduces to

$$r_e \int_0^a \chi_s(r_n) \chi_1(r_n) dr_n,$$

which vanishes by the orthogonality condition. Therefore, using again the orthogonality condition,

$$b_q = 16\pi^2 Q \varepsilon^2 \int_0^a \tau_1(r_e) \tau_q^*(r_e) r_e^2 dr_e \int_{r_e}^a \chi_s(r_n) \chi_1(r_n) dr_n \left\{ \frac{1}{r_n} - \frac{1}{r_e} \right\}. \quad (45)$$

Putting in the actual values of χ_s and χ_1 from § 3, case (i) for this simple case, namely,

$$\chi_s(r_n) = \frac{1}{(2\pi a)^{\frac{1}{2}}} \sin(\kappa_n r_n \sqrt{W_s}), \quad \chi_1(r_n) = \frac{1}{(2\pi a)^{\frac{1}{2}}} \sin(\kappa_n r_n \sqrt{W_1}),$$

allowing for the fact that we may treat r_e as small in the τ 's, and omitting factors of modulus unity, we find with sufficient accuracy that

$$|b_q| = \frac{8\pi}{a} Q \varepsilon^2 \cdot \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{\frac{1}{2}} \cdot \frac{\alpha}{\sqrt{(8\pi D)}} e^{i\pi\beta} \sqrt{\left\{ \frac{\pi\beta}{\sinh \pi\beta} \right\}} \\ \times \int_0^a r_e^2 dr_e \int_{r_e}^a \sin(\kappa_n r_n \sqrt{W_s}) \sin(\kappa_n r_n \sqrt{W_1}) \left\{ \frac{1}{r_n} - \frac{1}{r_e} \right\} dr_n.$$

The double integral reduces on integration by parts to

$$\frac{1}{6} \int_0^a r_n^2 \sin(\kappa_n r_n \sqrt{W_s}) \sin(\kappa_n r_n \sqrt{W_1}) dr_n,$$

and can then be evaluated, giving

$$\pm \frac{a}{6} \left[\frac{1}{\kappa_n^2 (\sqrt{W_s} - \sqrt{W_1})^2} - \frac{1}{\kappa_n^2 (\sqrt{W_s} + \sqrt{W_1})^2} \right].$$

For our model nucleus the second term is at least nine times smaller than the first and so may be neglected.

The value of

$$e^{i\pi\beta} \sqrt{\frac{\pi\beta}{\sinh \pi\beta}}$$

tends to unity as $\beta \rightarrow 0$; as $\beta \rightarrow \infty$ it behaves like $(2\pi\beta)^{\frac{1}{2}}$. The numbers in § 6 show that $\pi\beta$ is about unity for $V = 10^6$, but smaller for larger V . The V 's required are, however, not much larger than 10^6 , so that it is sufficiently accurate to take the value $(2\pi\beta)^{\frac{1}{2}}$ for this whole factor. We thus find

$$|b_q| = \frac{8\pi Q \varepsilon^2 (2\pi\beta)^{\frac{1}{2}}}{6\kappa_n^2 (\sqrt{W_s} - \sqrt{W_1})^2} \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{\frac{1}{2}} \frac{\alpha}{\sqrt{(8\pi D)}}. \quad (46)$$

Substituting this in (44) we find

$$\frac{W(t)}{t} = \frac{2\pi\alpha^2\beta}{9h^2} \left(\frac{Z}{a_0}\right)^3 \sqrt{\frac{2m_e}{E'}} \frac{8\pi^2 Q^2 \epsilon^4 a^4}{\kappa_n^4 (\sqrt{W_s} - \sqrt{W_1})^4 a^4}. \quad (47)$$

This gives the probability of interaction with one K-electron. It must be multiplied by 2 for the pair.

Applying the numerical values of § 6 and equation (20'), putting $Q = 2$, and multiplying by 2 as above, we obtain

$$\frac{W(t)}{t} = \frac{4 \times 10^{10}}{(\Delta s)^4}. \quad (48)$$

It is on the whole extremely probable that we should be dealing with a case of $\Delta s = -1$. Equation (48) then yields the value, 2.5×10^{-11} second, for the mean life of the nucleus against β -particle ejection which is quoted in the discussion in § 2. This yields a ratio for the number of 9.2 cm. α -particles to the number of 1.426×10^6 volt β -particles of 1/160 in excellent agreement with the observed 1/100.

It would not be correct to leave matters like this without referring to the value for ΔW_n given for our model nucleus in § 6. This is almost exactly correct (precisely 1.511×10^6 volts) if $\Delta(s^2) = 2^2 - 1^2$ and $a = 10^{-12}$ cm. We have, however, assumed $a = 2 \times 10^{-12}$ in the calculation of b_q . If we assume the value 10^{-12} which fits ΔW_n the value of the probability in (48) is reduced by a factor 16 and the ratio of α - to β -rays becomes 1/10 instead of the observed 1/100. Even this may be regarded as quite a satisfactory agreement for such a rough theory, but to accept this result as the best would be to take too unfavourable a view of the agreement. For if the potential walls are not indefinitely high we do find that effectively the energy levels may be determined by a value of a which is less than the effective value of a in b_q , though hardly by a factor so large as 2. It is, we think, fair to conclude that our theory yields good general agreement with observation.

§ 8. *Similar Collision Probabilities for L_I - and M_I -electrons.*—To calculate the similar probabilities for collisions with L_I - and M_I -electrons we have only to replace the $\tau_1(r_s)$ of (33) by the similar hydrogen functions for the 2s and 3s states. Since we have been able to put $r_s = 0$ in these functions, it is only necessary to compare their values at the origin. The comparison is given for example by Sommerfeld,* and shows that

$$\frac{\tau_{L_I}(0)}{\tau_K(0)} = \frac{1}{2\sqrt{2}}, \quad \frac{\tau_{M_I}(0)}{\tau_K(0)} = \frac{1}{3\sqrt{3}}, \dots$$

* Sommerfeld, 'Wellenmechanische Ergänzungsbänd,' p. 84.

Hence

$$W_K(t) : W_{L_I}(t) : W_{M_I}(t) : \dots = 1 : \frac{1}{8} : \frac{1}{24} : \dots$$

in surprisingly good agreement with observation, which gives* a ratio of 100 : 14 to compare with the theoretical 100 : 12½. The ratio for W_{M_I} is not well observed for these lines but in general an M_I -level β -ray line is about four times less intense than the corresponding L_I -level β -ray line. This is all the more satisfactory, since, so far as the rather uncertain observational evidence goes, the ratio of the observed absorptions in the K - and L_I -levels for a normal γ -ray is at least sometimes as great as 1/5·5 to 1/6 and seems to vary somewhat from line to line. But for a normal γ -ray one has no theoretical reason to expect these simple ratios to be repeated, since the important values of the functions $\tau(r_e)$ are not confined to $r_e = 0$.

§ 9. *The Evaluation of the Integral (32) when $C = \infty$ and the transition in l is $1 \rightarrow 0$.* As explained in the introduction, one of our objects has been to investigate whether the approximation of regarding the extension of the nucleus as indefinitely small will modify Miss Swirles's calculations to any serious extent, that is when the transition in the nucleus is allowed to be radiative by the selection rules, derived in the usual way for the dipole moment. As the result of our calculation is to justify Miss Swirles's approximation in this case it is unnecessary to evaluate the integral (32) in such a case exactly. It is sufficient to retain only such factors as can affect the ratio of the contributions from the two regions $r_e < a$ and $r_e > a$. The transition in l which we shall consider as a sufficient illustration is $1 \rightarrow 0$, which requires us to put $l_1 = 1$ in (32). We therefore take (32) with $l_1 = 1$, and insert in it values of $\chi(r_e)$ from § 3, of $\tau_q(r_e)$ from (39) and of $\tau_1(r_e)$ from (33), omitting any constant factors that we find it convenient to drop. We find

$$\begin{aligned} b_q \propto & \int_0^\infty e^{-r_e(\frac{Z}{a_e} + i\epsilon)} \frac{dr_e}{r_e} \cdot \frac{1}{2\pi i} \cdot \int_{i-\infty}^{i+\infty} \frac{\Gamma(s+i\beta) \Gamma(2-s)}{\Gamma(2+i\beta) \Gamma(2+s)} (-ixr_e)^s ds \\ & \times \left\{ \int_0^{r_e} (\kappa_n r_n \sqrt{W_s})^\dagger J_{\frac{1}{2}}(\kappa_n r_n \sqrt{W_s}) \sin(\kappa_n r_n \sqrt{W_1}) r_n dr_n \right. \\ & \quad \left. + r_e^3 \int_{r_e}^\infty (\kappa_n r_n \sqrt{W_s})^\dagger J_{\frac{1}{2}}(\kappa_n r_n \sqrt{W_s}) \sin(\kappa_n r_n \sqrt{W_1}) \frac{dr_n}{r_n^2} \right\}. \end{aligned}$$

This inner term $\{ \}$ is the correct form when $r_e < a$. When $r_e > a$ it is, of course, to be replaced by

$$\int_0^a (\kappa_n r_n \sqrt{W_s})^\dagger J_{\frac{1}{2}}(\kappa_n r_n \sqrt{W_s}) \sin(\kappa_n r_n \sqrt{W_1}) r_n dr_n.$$

* Ellis and Aston, *loc. cit.*

It will therefore be sufficient to compare the values of the two terms

$$\int_0^\infty e^{-r_s \left(\frac{Z}{a_s} + i\epsilon \right)} \frac{dr_s}{r_s} \cdot \frac{1}{2\pi i} \int_{\frac{1}{2} - \infty i}^{\frac{1}{2} + \infty i} \frac{\Gamma(s + i\beta) \Gamma(2 - s)}{\Gamma(2 + i\beta) \Gamma(2 + s)} (-i\alpha r_s)^s ds \\ \times \int_0^{r_s} (\kappa_n r_n \sqrt{W_s})^{\frac{1}{2}} J_{\frac{1}{2}}(\kappa_n r_n \sqrt{W_s}) \sin(\kappa_n r_n \sqrt{W_1}) r_n dr_n, \quad (49)$$

which represents in our approximation and notation the corresponding interaction integral of Miss Swirles's calculation, and the correct intranuclear part,

$$\int_0^a e^{-r_s \left(\frac{Z}{a_s} + i\epsilon \right)} \left\{ \frac{1}{2\pi i} \int_{\frac{1}{2} - \infty i}^{\frac{1}{2} + \infty i} \frac{\Gamma(s + i\beta) \Gamma(2 - s)}{\Gamma(2 + i\beta) \Gamma(2 + s)} (-i\alpha r_s)^s ds \right\} dr_s \\ \times \left\{ \frac{1}{r_s} \int_0^{r_s} (\kappa_n r_n \sqrt{W_s})^{\frac{1}{2}} J_{\frac{1}{2}}(\kappa_n r_n \sqrt{W_s}) \sin(\kappa_n r_n \sqrt{W_1}) r_n dr_n \right. \\ \left. + r_s^2 \int_{r_s}^a (\kappa_n r_n \sqrt{W_s})^{\frac{1}{2}} J_{\frac{1}{2}}(\kappa_n r_n \sqrt{W_s}) \sin(\kappa_n r_n \sqrt{W_1}) \frac{dr_n}{r_n^2} \right\}. \quad (50)$$

In (50) we may treat r_s as small, as before. Then the contour integral can be evaluated by bending the contour round so as to envelop the poles of $\Gamma(2 - s)$ which yields the series in ascending powers of r_s . We thus find

$$\frac{1}{2\pi i} \int_{\frac{1}{2} - \infty i}^{\frac{1}{2} + \infty i} \frac{\Gamma(s + i\beta) \Gamma(2 - s)}{\Gamma(2 + i\beta) \Gamma(2 + s)} (-i\alpha r_s)^s ds \sim -\frac{\alpha^2 r_s^2}{6}.$$

We are left with

$$\frac{\alpha^2}{6} \int_0^a dr_s \left\{ r_s \int_0^{r_s} (\kappa_n r_n \sqrt{W_s})^{\frac{1}{2}} J_{\frac{1}{2}}(\kappa_n r_n \sqrt{W_s}) \sin(\kappa_n r_n \sqrt{W_1}) r_n dr_n \right. \\ \left. + r_s^4 \int_{r_s}^a (\kappa_n r_n \sqrt{W_s})^{\frac{1}{2}} J_{\frac{1}{2}}(\kappa_n r_n \sqrt{W_s}) \sin(\kappa_n r_n \sqrt{W_1}) \frac{dr_n}{r_n^2} \right\}; \quad (51)$$

into this formula we put

$$\sqrt{x} J_{\frac{1}{2}}(x) \propto \frac{\sin x}{x} - \cos x;$$

we recall also that

$$\sin \kappa_n a \sqrt{W_1} = 0, \quad \frac{\sin(\kappa_n a \sqrt{W_s})}{\kappa_n a \sqrt{W_s}} = \cos(\kappa_n a \sqrt{W_s}).$$

We then find after many integrations by parts that (51) is sufficiently nearly equal to

$$\pm \frac{\alpha^2}{30} \frac{a^4 \sin(\kappa_n a \sqrt{W_s})}{\kappa_n^2 a^2 (\sqrt{W_s} - \sqrt{W_1})^2}. \quad (52)$$

During the process it is found incidentally that to the same approximation the last factor in (49) is

$$\frac{\frac{1}{2}a^2 \sin(\kappa_n a \sqrt{W_s})}{\kappa_n^2 a^2 (\sqrt{W_s} - \sqrt{W_1})^2}.$$

It is therefore sufficient to compare

$$\frac{1}{\Gamma} \alpha^2 a^2$$

for the intranuclear term, with

$$\int_0^\infty e^{-r} \left(\frac{Z}{a_0} + i\alpha \right) \left\{ \frac{1}{2\pi i} \int_{\frac{1}{2}-\infty i}^{\frac{1}{2}+\infty i} \frac{\Gamma(s+i\beta) \Gamma(2-s)}{\Gamma(2+i\beta) \Gamma(2+s)} (-i\alpha r)^s ds \right\} \frac{dr}{r},$$

for the ordinary radiative one. In this expression $-i\alpha$ means $e^{-i\pi} \alpha$, the integrals are absolutely convergent, and it can be shown that the order can be interchanged. The inner integral then becomes

$$\int_0^\infty e^{-r} \left(\frac{Z}{a_0} + i\alpha \right) r^{s-1} dr = \frac{\Gamma(s)}{\left(\frac{Z}{a_0} + \frac{1}{2}i\alpha \right)^s}.$$

The whole expression becomes

$$\frac{1}{2\pi i} \int_{\frac{1}{2}-\infty i}^{\frac{1}{2}+\infty i} \frac{\Gamma(s) \Gamma(s+i\beta) \Gamma(2-s)}{\Gamma(2+i\beta) \Gamma(2+s)} \left(\frac{-i\alpha}{\frac{Z}{a_0} + \frac{1}{2}i\alpha} \right)^s ds. \quad (53)$$

By expanding in powers of

$$\frac{i\alpha}{Z/a_0 + \frac{1}{2}i\alpha},$$

when this is small, bending the contour round the poles of $\Gamma(2-s)$, it is easily seen that (53) is equal to

$$\sum_{t=0}^{\infty} \frac{\Gamma(2+i\beta+t)}{\Gamma(2+i\beta)} \frac{(t+1)!}{t!(t+3)!} \left(\frac{i\alpha}{Z/a_0 + \frac{1}{2}i\alpha} \right)^{t+2},$$

which is an elementary function, easily shown to be equal to

$$\frac{\Gamma(-1+i\beta)}{\Gamma(2+i\beta)} \left\{ \frac{2}{\mu} [1 - (1-\mu)^{1-i\beta}] + (i\beta-1) [1 + (1-\mu)^{-i\beta}] \right\} \left(-\mu = \frac{e^{-i\pi} \alpha}{Z/a_0 + \frac{1}{2}e^{i\pi} \alpha} \right). \quad (54)$$

By analytic continuation the integral (53) will be equal to (54) for all values of μ such that $|\arg(-\mu)| < \pi$.

Since αa is about 0.2 for $a = 2 \times 10^{-12}$ cm., $\alpha a_0/Z$ is fairly large compared with unity. Hence in (54) we may put nearly enough

$$-\mu = 2e^{-\pi i},$$

and (54) becomes approximately

$$-\frac{1 + e^{-\pi\beta}}{(1 + \beta^2)}, \quad (55)$$

which we see on referring to § 6 is of order unity. But since αa is about 0.2

$$\frac{1}{15}\alpha^2 a^2 = 0.003,$$

which is negligible compared with unity, so that Miss Swirles's approximation is justified.

It seems unnecessary, therefore, to pursue such calculations of intranuclear corrections any further, except as above when the dipole moment actually vanishes.

§ 10. *Nuclear Models with finite height of the Potential Barrier.*—It remains only to verify the statements of § 2 that a finite height of the barrier cannot seriously increase the effective extension of the nucleus from the point of view of collisions with the K-electron. The wave-function ($l = 0$) is now given by the equations (22) and (23), namely

$$\begin{aligned} \psi &= \frac{A}{r_n} \sinh(\kappa_n r_n \sqrt{W_s}) & (r < a), \\ \psi &= (-)^{s-1} \sqrt{\left(\frac{W_s}{C}\right)} \frac{A}{r_n} e^{-\kappa_n(r_n-a)} \sqrt{(C-W_s)} & (r > a). \end{aligned}$$

It is unnecessary to go through the calculations in detail. One can see at once that the *order* of the effect in § 7 must be to add to

$$\frac{1}{8} \int_0^a r_n^2 \sin(\kappa_n r_n \sqrt{W_s}) \sin(\kappa_n r_n \sqrt{W_1}) dr_n$$

a term of the order (very roughly)

$$\frac{1}{8} \sqrt{\left(\frac{W_s W_1}{C^2}\right)} \int_a^\infty r_n^2 e^{-\kappa_n(r_n-a)} [\sqrt{(C-W_s)} + \sqrt{(C-W_1)}] dr_n. \quad (56)$$

The order of the original term is

$$\frac{1}{8} \frac{a^3}{\kappa_n^2 a^2 (\sqrt{W_s} - \sqrt{W_1})^2} \quad \text{or} \quad \frac{a^3}{6\pi^2 (\Delta s)^2};$$

the best that the new term can do is to have C and W_1 nearly equal. It is then approximately

$$\frac{a^3}{6\kappa_n a \sqrt{W_1 - W_s}}.$$

When $a = 10^{-12}$ and $W_1 - W_s = 1.426 \times 10^6$ volts this becomes

$$\frac{a^3}{6 \times 5},$$

which is about twice as big as our original term. Thus in an extreme case the finite height of a barrier might allow the wave-functions to spread so much that the total collision term in b_q is about three times as large as we have calculated. Some such effect may well come in and close up the residual numerical discrepancies left over in §7. When, however, we compare with §9 we see that no such correction is large enough to make the intranuclear term comparable with the radiative term; moreover, since $\kappa_n \sqrt{(W_s - W_1)} = 5/a$ about, the product of the wave-functions outside the nucleus dies away at slowest like

$$e^{-5r/a},$$

and will not survive far enough out from the nucleus to affect the calculation of the radiative term itself.

If it is desired to look further into possible effects of a finite barrier it must be remembered that all the calculations of this section are extremely rough and that no pretence has been made at showing more than order of magnitude. The rough comparisons given here are not intended to do more than suggest that detailed investigation of finite barriers as a possible source for the required correction factor of 10 in Miss Swirles's calculations is not likely to be profitable. As we have already explained in §2 almost anything can happen if in the collision the kinetic energy of oscillation of the α -particle is unchanged, so that in (56) both W_s and W_1 are nearly equal to C, while the electron takes up internal energy from some structure in the oscillating α -particle; but we shall not pursue this matter further here.

*The Application of Osborne Reynolds' Theory of Heat Transfer to
Flow through a Pipe.*

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In a recent paper Messrs. Eagle and Ferguson* describe a very complete series of measurements of the conditions of heat transfer between a brass tube and water flowing through it. They base the discussion of their results on Osborne Reynolds theory of heat transfer according to which there is a complete analogy between the transfer of heat and momentum so that if a hot sheet is moved edgewise through a fluid the distributions of temperature and momentum in the water are identical. The assumption underlying the theory is that any portion of the fluid which comes sufficiently near the heated surface to be moved forward with the speed of the hot surface is also heated to the temperature of that surface, or, alternatively, a portion which is moved forward at a fraction, β , times the speed of the plate is also heated through a temperature equal to β times the difference in temperature between the plate and the fluid. In this manner Reynolds' theoretical coefficient† of heat transfer, κ_R , may be calculated. The observed heat transfer coefficient is represented by Messrs. Eagle and Ferguson as κ_0 and their results are expressed in the form $F = \kappa_R/\kappa_0$ where F is a fraction determined under a variety of different conditions of experiment.

This crude form of Reynolds' theory suffers from two possible main sources of error, (A) the heated surface may raise the velocity of any portion of the fluid near it through a greater fraction of its own velocity than it raises the temperature expressed as a fraction of its own temperature, the initial temperature of the fluid being taken as zero. This might be expected to give rise to large errors in cases where the thermal conductivity is specially low. (B) The effect of local pressure differences which are inherent in all turbulent motion and alter the momentum of the fluid at any point without altering its temperature is neglected. The essential assumption in Reynolds' theory is that these local pressure differences have no effect on the average distribution of velocity.

* 'Proc. Roy. Soc.,' vol. 127, p. 540 (1930).

† The coefficient of heat transfer is defined as (heat flow per square centimetre)/(temperature difference between fluid and inside surface of tube).

Messrs. Eagle and Ferguson allow for (A) by expressing F in the form

$$F = \alpha + \beta(\sigma - 1) + \gamma(\sigma - 1)^2, \quad (1)$$

where $\sigma = \mu s/c$ and α , β and γ are the same for all fluids, depending only on Reynolds' number $\tau = \rho v d/\mu$ where d is the diameter of the pipe and v the velocity, ρ the density of the fluid, μ is the viscosity, s the specific heat and c the thermal conductivity. In the particular case when $\sigma = 1$ which is not very far from the case for gases, $F = \alpha$. In this case Reynolds' expression for heat dissipation should be correct even although the effect of the laminar layer at the surface is taken into account,* provided (a) Reynolds' theory is true, and (b) the theory is directly applicable to the conditions of Messrs. Eagle and Ferguson's experiment. When $\sigma = 1$ therefore, F should be equal to 1 for all values of τ ; so that α should be equal to 1 for all values of τ and σ , and the fact that their experiments give values of α varying from 1.04 for $\tau \rightarrow \infty$ to 1.48 for $\log \tau = 3.7$, while their calculation shows that $\alpha = \beta = 11/6$ as $\tau \rightarrow 0$ leads them to the conclusion that "when turbulence is feeble the thermal resistance of the fluid is much larger than is given by Reynolds' theory."

This result is in contradiction to other recent experiments—particularly those of Sir Thomas Stanton who found in his experiments with a flat ring-shaped surface that for air F is less than 1 even when the maximum possible allowance has been made for conditions in the laminar layer.

Discussion of Messrs. Eagle and Ferguson's Experiments.

It seems that even if Reynolds' theory is true there are two reasons, connected with the experimental conditions under which Messrs. Eagle and Ferguson's experiments were carried out, why they should not obtain experimentally the value $\alpha = 1$, so that their conclusion that "the thermal resistance is much larger than is given by Reynolds' theory," cannot be accepted as a result of their experiments. These two reasons are:—

(A) The experiments were carried out under conditions to which Reynolds' theory is not directly applicable. In order that a complete analogy between the transfer of heat and of momentum may exist, not only must heat and momentum be transferred from layer to layer through the fluid by the same masses of fluid, but the rates at which heat and momentum are communicated to portions of the fluid by external agencies must be related to one another. In the case of flow under pressure through a heated pipe momentum is being

* It should even be true for the case of steady viscous flow.

communicated at a uniform rate throughout the fluid, while heat in Messrs. Eagle and Ferguson's experiments was communicated to the fluid only through the walls. In order that Reynolds' theory may be applicable to flow under pressure through a pipe the heat must be communicated uniformly through the mass. Such a condition could, of course, be realised, at any rate theoretically, by using a conducting fluid passing through a tube which was a conductor of heat but a non-conductor of electricity. A heating current passing through this fluid would supply the heat in the correct manner if the temperature of the tube were maintained constant throughout its length.

(B) Even if Reynolds' theory could be directly applied to the conditions of heating used by Messrs. Eagle and Ferguson their method of measuring mean temperature at any section of the pipe is such that Reynolds' theory could not be applied to their results. They allow the heated water to flow into a chamber where, presumably, complete mixture takes place. Taking the temperature of the walls as zero, if θ is the temperature at any radius, their mean is

$$\theta_M = \frac{2}{a^2 u_m} \int_0^a u \theta r dr \text{ where } u \text{ is the velocity at radius } r \text{ and } u_m \text{ is the mean velocity.}$$

In cases like that of flow through a pipe where θ and u rise and fall together this is greater than the true mean temperature over the section, which

$$\text{is } \theta_m = \frac{2}{a^2} \int_0^a \theta r dr. \text{ In cases to which Reynolds' theory applies } \theta \text{ and } u \text{ are}$$

everywhere proportional to one another so that the mean temperature must be obtained in the same way as the mean velocity. The mean velocity is

$$u_m = \frac{2}{a^2} \int_0^a u r dr \text{ so that } u_m \text{ is comparable with } \theta_m \text{ and not with } \theta_M.$$

Case of Viscous Flow.

In the case of viscous flow for which the heat transfer values are readily calculable it is possible to calculate the value of α which would be found in experiments conducted by the methods of Messrs. Eagle and Ferguson, in fact they have already done so. They find $F = \alpha + \beta(1 - \sigma) + \gamma(1 - \sigma)^2 = 11\sigma/6$ so that $\alpha = 11/6$, $\beta = 11/6$, $\gamma = 0$. If θ_1 and u_1 are the temperature and velocity of the fluid at the centre of the pipe, I find $\theta_m/\theta_1 = 4/9$, $\theta_M/\theta_1 = 11/18$, $u_m/u_1 = \frac{1}{2}$, $F = 3\sigma/2 (\theta_m/\theta_1) (u_1/u_m)$, so that if θ_m had been used instead of θ_M it would have been found that $F = 3/2 (2) (4/9)\sigma = 4\sigma/3$, so that the use of θ_M instead of θ_m raises α in the ratio 11 : 8.

If the experiment had been conducted in such a manner that Reynolds' theory is directly applicable, *i.e.*, the heating had been by an electric current

through the fluid instead of through the containing tube, then it is a simple matter to show that $F = \sigma \frac{\theta_m}{\theta_1} \frac{u_1}{u_m}$, and in this case $\theta_m = \frac{1}{2}\theta_1$, while $u_m = \frac{1}{2}u_1$, so that, and for this case, $\alpha = \beta = 1$, $\gamma = 0$. In the case of viscous motion at any rate, experiments carried out in such a manner that Reynolds' theory is directly applicable would therefore yield the result that $\alpha = 1$, and the heat dissipated would be exactly the amount given by Reynolds' expression. The difference between heat dissipated in Messrs. Eagle and Ferguson's experiments and that calculated by Reynolds' expression are therefore entirely accounted for at low values of τ , by the incorrect application of Reynolds'* theory and by their method of estimating the average temperature of water which is not that contemplated in Reynolds' theory.

Application of Reynolds' Theory for Higher Values of Reynolds' Number.

Though it is not possible to apply Reynolds' theory directly to experiments conducted on the manner of Messrs. Eagle and Ferguson because the heat and momentum transfer are not proportional to one another, it seems worth while to calculate what heat transference might be expected in such experiments if it is assumed that

$$\frac{h}{m} = S \frac{\partial \theta}{\partial r} / \frac{\partial u}{\partial r}, \quad (2)$$

where S is the specific heat, m is the rate of momentum transfer across unit area and h the heat transfer, h and m are both functions of r , the distance from the centre of the tube. This formula (2) is the form which expresses Reynolds' theory when the additional assumption is made that the "mixture length" is small compared with the radius of the tube. The "mixture length" is in this case the radial distance through which any portion of air preserves its temperature and momentum till it mixes with its surroundings.

The equation of motion for fluid flowing under a pressure gradient P in a circular pipe is

$$\frac{\partial}{\partial r} (rm) = rP. \quad (3)$$

The equation for heat flow under the conditions of Messrs. Eagle and Ferguson's

* It seems that Reynolds himself hardly recognised the error involved in applying his theory to the case of pressure flow through pipes.

experiments in which the temperature rises at a uniform rate of g degrees per centimetre of pipe is

$$\frac{\partial}{\partial r}(rh) = \rho s u r g, \quad (4)$$

integrating (3),

$$m = \frac{1}{2} Pr;$$

integrating (4),

$$vh = \rho s g \int_0^r u r dr,$$

which can be put in the form

$$\frac{h}{\rho g s u_1 r} = \frac{1}{r^2} \int_0^r \left(\frac{u}{u_1} \right) r dr. \quad (5)$$

We may apply (5) to find the rate of heat transfer at any radius when the distribution of velocity across the section of the pipe is known. Taking the case given by Stanton* of a stream of air flowing through a pipe 7.4 cm. diameter with velocity $u_1 = 2215$ cm. per second at the centre, corresponding values of r/a and u/u_1 are given in columns 1 and 2 of Table I. From these the values of $h/(\rho g s u_1 r)$ were calculated by means of (5) and these are given in column 3.

Table I.

1.	2.	3.	4.	5.
$\frac{r}{a}$	$\frac{u}{u_1}$	$\frac{h}{\rho g s u_1 r}$	$\int \frac{h}{\rho g s u_1 r} \frac{du}{u_1}$	$\frac{\theta}{\theta_1}$
0.0	1.000	0.500	0.000	1.000
0.1	0.995	0.499	0.00250	0.9941
0.2	0.982	0.497	0.00898	0.9790
0.3	0.966	0.492	0.01684	0.9614
0.4	0.944	0.487	0.02756	0.9353
0.5	0.916	0.479	0.04098	0.9040
0.6	0.882	0.470	0.05696	0.8665
0.7	0.844	0.460	0.07444	0.8255
0.8	0.794	0.448	0.09684	0.7730
0.85	0.764	0.441	0.11007	0.7419
0.9	0.722	0.434	0.12829	0.6990
0.95	0.664	0.424	0.15291	0.6435
0.98	0.596	0.418	0.18131	0.5750
0.99	0.548	0.415	0.20123	0.5285
1.00	0	0.411	0.42643	0

So far no use has been made of Reynolds' theory. Substituting $\frac{1}{2}Pr$ for m in (2) the connection between θ and r is

$$\frac{\partial \theta}{\partial r} = \frac{2h}{sPr} \frac{\partial u}{\partial r}. \quad (6)$$

* "The mechanical viscosity of fluids," 'Proc. Roy. Soc.,' A, vol. 85, p. 367 (1911).

Hence

$$\theta - \theta_1 = \frac{2}{P_8} \int_0^r \frac{h}{r} \frac{\partial u}{\partial r} dr$$

or

$$\theta - \theta_1 = \frac{2\rho g u_1^2}{P} \int_{u_1}^u \frac{h}{\rho g s u_1 r} d\left(\frac{u}{u_1}\right). \quad (7)$$

The values of the integral in (7) can be found from the figures in columns 2 and 3 of Table I. It is given in column 4. If θ is the amount by which the temperature at radius r exceeds that of the inner surface of the wall of the pipe at the same section, and θ_1 is the value of θ at the centre of the pipe, θ/θ_1 can be found by dividing the figures in column 4 by 0.4264 and subtracting the result from unity. These are given in column 5. If H is the rate of heat transfer at the surface and R the friction $R = \frac{1}{2}Pa$ and $H/(\rho g s u_1 a) = 0.411$ (see last figure column 3, Table I) hence

$$\frac{H}{R} = \frac{2\rho g s u_1}{P} (0.411),$$

but

$$\theta_1 = \frac{2\rho g u_1^2}{P} (0.4264)$$

(see last figure, column 4). Hence

$$\frac{H}{R} = \frac{0.411}{0.4264} \frac{s\theta_1}{u_1} = 0.964 \frac{s\theta_1}{u_1}. \quad (8)$$

It now remains to evaluate θ_M , θ_m and u_m from the figures given in Table I.

$$\frac{u_m}{u_1} = \frac{2}{a^2} \int_0^a \left(\frac{u}{u_1}\right) r dr = 2(0.411)^* = 0.822.$$

By graphical integration I find $\theta_m = 0.801 \theta_1$, $\theta_M = 0.823 \theta_1$. Hence

$$\frac{H}{R} = (0.964) \left(\frac{0.822}{0.823}\right) \frac{s\theta_M}{u_m} = 0.963 \frac{s\theta_M}{u_m}.$$

Hence the value for α which this application of Reynolds' theory would lead one to expect in Messrs. Eagle and Ferguson's experiment is $(0.963)^{-1} = 1.04$.

The observed value of α for $\tau = 10^5$ (corresponding with the value appropriate to Stanton's measurement) is given in their table as 1.075. It appears, therefore, that for this value of τ a more complete application of Reynolds' theory is capable of accounting for 4 out of the 7½ per cent. by which their observed value of the heat transfer falls short of that given by the crude application of Reynolds' formula.

* See last figure, column 3, Table I.

On the Spectroscopy of Auroral Green Line Radiation.

By J. C. McLENNAN, F.R.S., and H. J. C. IRETON, M.A.

(Received June 26, 1930.)

[PLATES 1, 2.]

I. SPECTROSCOPY.

In a recent paper* by the authors on "Spectroscopy of the Light from the Night Sky," a description was given of the development and the construction, with optical details, of a high light power spectrograph suitable for photographing the spectrum of the light of the moonless night sky and the spectra of auroral displays.

Preliminary experiments were carried out with this instrument in England and in Canada, and a considerable number of spectrograms recorded with the instrument were reproduced and included in the paper.

In taking these spectrograms the camera lens used in the spectrograph was a compound F/1 lens of 50 mm. focus that had four components and was made by Messrs. Ross, of London.

Quite recently we were able to secure two additional camera lenses for use with the spectrograph. These each consisted of one single aspherical component designed to give the maximum concentration of light for radiation in the neighbourhood of $\lambda 5577$, the auroral green line. All three of these lenses have been subjected to comparative tests and the results are recorded below. A brief description of the spectrograph itself is included.

The Spectrograph.

The spectrograph as supported when photographing the spectrum of the light of the night sky is shown in fig. 1 (Plate 1). In the spectrography of extended light sources such as the sky, the focal length of the collimator lens has no direct effect on the "speed" of the spectrograph. In order that the whole aperture of a lens of very short focal length may be effective special attention requires to be paid to the jaws of the slit to make certain that they do not obstruct light passing through them at high obliquity. It is a matter of convenience therefore to use a collimator lens of long focus, say, of not less than 10 times the effective aperture. It is desirable too that the slit used

* 'Can. J. Res.,' vol. 2, p. 279 (1930).

should not be too narrow or the individual grains of the photographic plate might not be fully illuminated. This, of course, can be simply remedied by widening the slit. The factors of prime importance to be observed in the design of a spectrograph of high light power are "A," the effective area of the camera lens as limited by the prism and F, its focal length. If loss of light by absorption and reflection be ignored the relative speeds of spectrographs intended for the photography of well separated bright lines are given by the expression A/F .

With the spectrograph shown in fig. 1 the dispersion was obtained by the use of a 60° prism. This prism had a length of face of 127 mm. and a height of 75 mm. and it was made by Messrs. Chance from glass of melt No. B.L.F. 4628. The refractive indices of the glass as given by the makers were :—

$$\mu_G = 1.57958$$

$$\mu_D = 1.58320$$

$$\mu_F = 1.59200$$

$$\mu_G' = 1.59932$$

The collimator lens was an achromatic cemented doublet of 50 mm. aperture and 56 cm. focus. The effective length of the slit could be varied by means of an aperture wedge up to a maximum of 18 mm. The slit itself was mounted in a draw tube having a 50 mm. rack and pinion focussing motion. Two plate holders were provided with the instrument, with the one, plates approximately 108 mm. $\times$ 82.5 mm. could be used and with the other small plates 60 mm. $\times$ 45 mm. In our work only the latter plate holder was used. It was provided with three point supports, one of which was on a cam-like disc that enabled one to alter at will within limits the tilt of the plate. This device was found to be extremely useful when focussing up the full spectrum with the different camera lenses.

The Camera Lenses.

(A) *The Ross Lens.*—The first camera lens used was a compound one that had four components and was designed in accordance with a formula by Mr. T. Smith, of the National Physical Laboratory, Teddington. Its characteristic features are shown in figs. 2 and 3. The focal lengths of the component lenses are as follows :—

Lens (1) 208.0 mm.

„ (2) 213.4 „

„ (3) 195.9 „

„ (4) 190.0 „

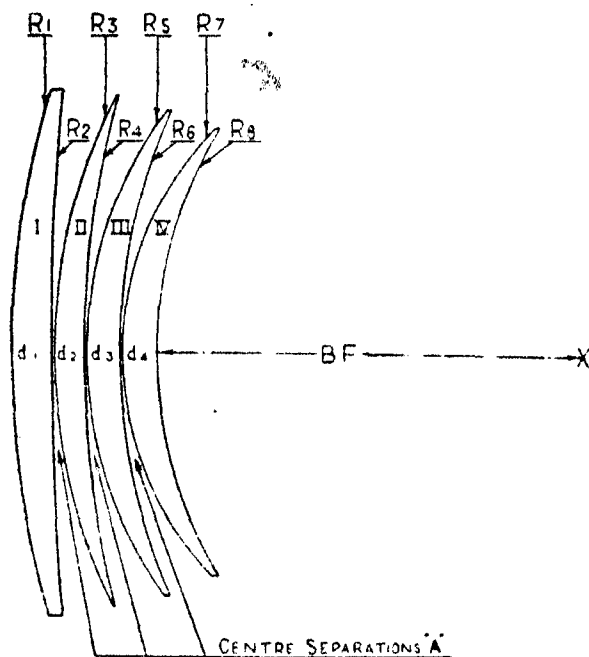


FIG. 2.—2" F 1.0 Lens.

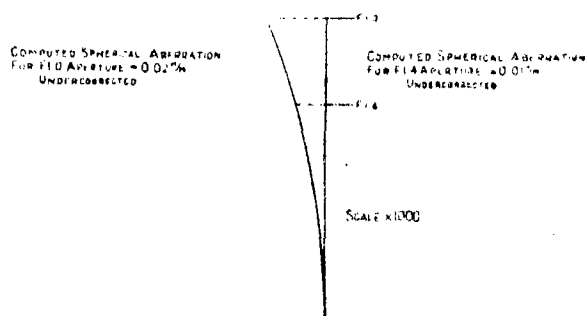


FIG. 3.—Characteristic Features of the F/1 Lens used.

The angular field was about 10 degrees and the size of "plate covered" with it was 8.5 mm. diagonal. This lens was constructed by Messrs. Ross in accordance with the results of the final calculations ordinarily made by them to adapt their lenses to the refractive indices of the glasses used. The refractive indices of the four samples of glass used in the construction of the lens are for the mercury green line $\lambda 5461$ as follows:—

- (1) 1.61491
- (2) 1.58631
- (3) 1.61491
- (4) 1.58131

The residual spherical aberration over the whole of the aperture was removed by Messrs. Ross and the figuring was done with the lens *in situ* in a lens testing interferometer. The correction made to within a quarter of a wave-length was carried out with the light of the green line λ 5461.

(B) *The Mellish Lens*.—This lens consisted of a single component kindly ground for us with aspherical surfaces by John E. Mellish, of St. Charles, Illinois, U.S.A. The glass was supplied by The Adam Hilger Company from melt No. B.S.C. 3454. Its specific gravity was 2.54 and its refractive indices were given us as follows :—

$$\begin{aligned}\mu_C &= 1.51051 \\ \mu_{C-D} &= 0.00239 \\ \mu_D &= 1.51290 \\ \mu_{D-F} &= 0.00568 \\ \mu_F &= 1.51858 \\ \mu_{F-G} &= 0.00452 \\ \mu_G &= 1.52310\end{aligned}$$

The focal length of this lens was 43.2 mm. for λ 5000 and its diameter 57.15 mm. Its angular field was 6.5° and the "plate covered" with it was 4.8 mm. In this specification of the photographic "plate covered" the datum is based upon the actual length of spectrum appearing on the plate and not on the actual definition of the image or its variation on passing from the axial image. This procedure is necessitated by the fact that the general standard of definition rather than the variation of such over the field is the characteristic of the performance of the lens which is mainly apparent on testing it. This lens on examination showed a slight "stepping" or corrugation of its surface after the manner of a lighthouse lens, and it is probable that this may be taken as an indication of the mode of testing and correcting employed by Mellish.

(C) *The Hilger Lens*.—This lens also consisted of a single aspherical component and was made by The Adam Hilger Company from glass designated as melt No. M.B.C. 3257. Its refractive indices were given as :—

$$\begin{aligned}\mu_C &= 1.57247 \\ \mu_D &= 1.57540 \\ \mu_F &= 1.58248 \\ \mu_G &= 1.58823\end{aligned}$$

The focal length of the lens was 55.63 mm. for λ 5000 and its diameter was the same as that of the Mellish lens namely 57.15 mm. The "plate covered" with it was 6.35 mm. and its angular field was 6.5°. In the making of this

lens the figuring was controlled by one of Twyman's* lens testing interferometers.

Photographic Plates and other Details.

The object we had in mind in developing a high light power spectrograph was to reduce as much as possible the time required to secure well-marked and clearly-defined lines in spectrograms taken of the light from the moonless cloudless night sky and of that emitted in displays of polar auroræ. It is desirable to investigate the variations in the intensity of the non-polar auroral light that occurs in the course of a single night with a view to accounting for the maximum that this intensity is known to reach about an hour after midnight. It is also desirable to study the relative intensities of the spectral lines that appear in spectrograms of the polar auroræ with a view to gaining information about the amount of nitrogen and of oxygen present in the upper atmosphere at different heights above the earth and in regard to the state in which these gases exist at these high levels. It is also desirable to learn something about the temperatures prevailing at these heights in the upper atmosphere and information on this point may perhaps be derivable from the half widths of the spectral lines that originate in the light of the polar auroral. For all these purposes a spectrograph of the highest light power and capable of giving sharply-defined spectral lines is a prime necessity. Even when such an instrument is available further progress, we have found, can still be made by increasing the sensitivity of the photographic plates used in recording the spectra. We have made an exhaustive study of all types of photographic plates on the market or that have been specially made up for us up to the present time, and while good results can be obtained with several types of plate, Cramer's so-called iso-instantaneous plates are the ones that we have found to be by far the most sensitive to the light of the auroral green line. They are manufactured by The G. Cramer Dry Plate Company, of St. Louis, U.S.A. It may be stated here that in using these plates with the spectrograph described above, we found that the strongest and most clearly defined records of the non-polar auroral green spectral line were obtained when a spectrographic slit width of 1 mm. was used.

Selected Observations made with the Ross Camera Lens.

(1) In our observations with the night sky light spectrograph we have found that the intensity of the non-polar radiation corresponding to the auroral

* Twyman, 'Phil. Mag.', vol. 35, p. 49 (1918).

green line coming to earth from a moonless cloudless sky was roughly the same whether the observations were made at ground level in the south of England, and in Ontario, and Saskatchewan, Canada, or at an elevation of 2300 metres above sea level on Sulphur Mountain at Banff in Alberta, Canada. At all of these stations detectable records of the non-polar auroral green spectral line were obtained with the Ross camera lens when exposures having a duration of 10 to 20 minutes were made. Three reproductions five times enlarged of spectrograms taken with the object of ascertaining the shortest time of exposure required to obtain a visibly perceptible record of the non-polar auroral green spectral line with the light from the moonless night sky are shown in fig. 4 (Plate 1). These were taken after evening twilight on Sulphur Mountain, Alberta, during the early portion of the night of November 5, 1929. The exposure for the first one, A, began at 7.30 p.m. and lasted for 10 minutes. That for the second, B, began at 7.40 p.m. and lasted for 15 minutes, while that for the third, C, began at 7.55 p.m. and lasted for 20 minutes. It will be seen that each of the reproductions shows the wave-length at λ 5577 and no other wave-lengths. Spectrogram A shows the line λ 5577 faintly but quite definitely, which makes it clear that with the Ross camera lens in the spectrograph we were able to obtain a perceptibly visible record of the green line radiation of the non-polar night sky light in as short a time as 10 minutes. The exposures were made, it should be added, after the moon had set.

(2) In fig. 5 (Plate 1) there are shown reproductions about 12 times enlarged of five spectrograms taken of the auroral green line radiation from the moonless night sky on September 10-11, 1929, on the grounds of the Wentworth Dormy House Club, at Virginia Water, England. Each exposure was of 1 hour's duration and the width of slit used was 1 mm. The moon set at about 10 o'clock on September 10. The exposure for A was from 11.45 p.m. on the 10th to 12.45 a.m. on the 11th, that for B from 12.45 a.m. to 1.45 a.m., for C from 1.45 a.m. to 2.45 a.m., for D from 2.45 a.m. to 3.45 a.m., and for E from 3.45 a.m. to 4.45 a.m. Tracings that were taken with a Moll spectrophotometer showed that of the five spectral lines recorded, the one obtained for the period 1.45 a.m. to 2.45 a.m., namely C, was the strongest. As the times recorded here were for the season of the year when the Daylight Saving Bill was in operation, the records supplied by fig. 5 go to support the view already put forward by McLennan, Ireton and McLeod and independently by Lord Rayleigh that the non-polar auroral green line radiation from the moonless night sky acquires a maximum intensity shortly after midnight.

(3) The spectrograph when equipped with the Ross compound lens was used

on a number of occasions to photograph the spectrum of the light of the polar aurora. The reproductions enlarged about 12 times of a set of spectrograms taken on Sulphur Mountain during an auroral display on the night of November 2-3, 1929, are shown in fig. 6 (Plate 1). In this display there was an intense illumination extending over the whole northern half of the sky. Superimposed on this background occasional streamers shot up from the horizon towards the zenith. They could be observed at various times in different positions over an area extending from the north-west to the north-east. None of these streamers appeared to have a duration of more than a few minutes.

All the exposures for the spectrograms used in preparing fig. 6 were made between 3.08 a.m. and 4.30 a.m. on November 3 with the spectrograph pointing to the north star and with a slit width of 1 mm. For A the exposure was 5 minutes, for B 10 minutes, for C 15 minutes, for D 20 minutes, and for E 30 minutes. In all the spectrograms the oxygen auroral green line $\lambda 5577$ and the nitrogen bands $\lambda 4278$ and $\lambda 3914$ were distinctly recorded.

The originals of C, D and E on close examination showed six other bands recorded faintly. In the reproduction E they can be seen but not very distinctly at the points indicated by arrows. The reproduction E serves to show very clearly the needs still to be met in spectroscopy of the auroral light. What is required is to bring out not only the three strong lines, but all the lines appearing on E with the greatest clearness and with exposures of the shortest duration possible. With this end in view our efforts were directed towards securing single component camera lenses having high light power and giving a clearly-defined spectrum over as wide a range of wave-lengths as possible. An account of some preliminary results we have been able to secure with such lenses is given in what follows.

Comparison of Ross, Mellish and Hilger Lenses.

The Mellish and Hilger single component lenses did not become available until about the middle of May, and as the nights were then approaching the time of their shortest duration it was obviously not a very suitable time for making comparative tests of the camera lenses by taking spectrograms with them of the light from the moonless cloudless night sky. Recourse was, therefore, had to an experimental test carried out in the laboratory. The lenses in their mounts were in turn inserted in the spectrograph and with each the adjustments were noted that were necessary to obtain the best focussed and the best and most clearly-defined spectrum of the light from a helium filled Geissler tube excited by the current from a small transformer and operated

under fixed conditions. The time of exposure in each case was one second and the width of slit used was in each case the same and less than 0.01 mm. An illustration of the spectrum of this light obtained with each of the camera lenses inserted in turn in the spectrograph is shown in fig. 7 (Plate 2). All three lenses were of course corrected so as to give best effects with light of wave-length approximately equal to $\lambda 5577$. The dispersion with the Ross and Hilger lenses was approximately the same and greater than that obtained with the Mellish lens.

The Ross lens it will be seen gave a spectrum well defined for $\lambda 5876$ to $\lambda 3613$. While the spectral lines $\lambda 5876$ and $\lambda 5016$ were the more sharply defined in the Ross lens spectrum, it will be readily seen that the intensities of these lines in the Hilger and Mellish lens spectra are greater than the intensities of the same spectral lines in the spectrum of the Ross lens. It follows, therefore, that with either the Mellish or the Hilger single component camera lens inserted in the spectrograph the instrument will have more light power and be considerably "faster" than if the Ross compound lens be used with it. It is estimated that the Hilger or the Mellish single component lens will be found to be approximately more than 25 per cent. faster than the Ross compound one. With the latter the corrections for aberration were effected by the use of eight glass air surfaces and naturally it could not be as effective where the night sky line alone was concerned as a single lens in which the spherical aberration was corrected by retouching.

Although the season of the year and the time of the month was not very suitable for it a test was made as to the relative merits of the Hilger and Mellish single component lenses for work on the light of the night sky by taking spectrograms with each in the spectrograph in turn of the non-polar auroral light on the night of June 15 last the observing station being the one at Virginia Water used in last year's experiments. On this night the sun set at 9.16 p.m. and the moon rose at 12.23 a.m. of the following morning. An exposure was made with the Hilger lens between 11.05 p.m. and 11.35 p.m. and this was followed by one with the Mellish lens from 11.50 p.m. to 12.20 a.m. Reproductions five times enlarged of these spectrograms are shown in figs. 8 and 9 (Plate 2). In the spectra obtained with both lenses it will be seen that in addition to the $\lambda 5577$ there is a broad band on the short wave-length side of it. This band has always been obtained with light from the moonlit sky and was no doubt in this case due to the twilight that continued to illuminate the sky faintly throughout the night.

While the Mellish lens shows in use an advantage over the Ross compound

lens for photography of the night sky spectral line, there is, as fig. 9 shows, a considerable scatter of light with the use of it in the spectrograph. The difficulty of figuring a lens of such large aperture will be realised when it is pointed out that local departures from sphericity have to be made amounting to at least 0.5 mm. It is not surprising therefore to find that the Mellish lens exhibits a certain amount of corrugation and stepping of its surface which produces scatter and prevents the performance being as good as it otherwise would be.

With the Hilger single component lens in the spectrograph it will be seen from fig. 8 that there is practically no scatter. There is, moreover, considerable improvement in brightness and definition, all of which was no doubt due to the fact that the figuring was controlled by the use of the Twyman lens testing interferometer. Both the Mellish and Hilger lenses were, of course, corrected for the neighbourhood of the night sky line and the definition for the outlying parts of the spectrum is therefore very inferior to that of the Ross lens. It is only for spectral lines in the neighbourhood of $\lambda 5577$ that they show an advantage. It would appear then that in the photography of the whole spectrum from $\lambda 5876$ to $\lambda 3613$ the best results attainable by us for the present can be obtained only by the use of the Ross compound camera lens or one like it in the spectrograph. For the photography of the spectral line corresponding to the green radiation of wave-length $\lambda 5577$ of the polar and non-polar auroræ our results go to show that in order to obtain a visibly perceptible and clearly-defined record the Hilger single component lens could be used with half the exposure required by the Mellish lens and approximately only 60 per cent. of that required by the Ross compound lens.

II. AURORAL GREEN LINE RADIATION.

As a result of careful observation and study it is now generally conceded that the most characteristic and possibly only feature of the spectrum of the light from the moonless night sky when unilluminated by any sunlight is a faint yellow-green spectral line that has been identified with the green line at $\lambda 5577.341$ in the spectrum of the light of the polar aurora. This line was shown by McLennan and Shrum to belong to the spectrum of atomic oxygen, and it is now known as a result of observations made by McLennan, McLeod and Ruedy on its Zeeman effect that it originates in transitions of oxygen atoms from a $^1S_0$ metastable energy state to another metastable one designated as $^1D_2$.

Up to the present it has not been possible to obtain in laboratory experi-

ments an exact replica of this spectrum of oxygen obtainable with the light from the moonless and non-sunlit night sky.

We recently turned our attention to this matter however, and with the kind assistance of Mr. R. H. Chappell, Glassblower to the Physical Laboratory at Toronto, and of one of our research workers, Mr. Moles, we were enabled to make some progress in this direction.

In our earlier experiments the glass tubes used for holding the gas through which an electrical discharge was passed to produce the green line radiation λ 5577-341 were generally provided with two sets of electrodes, one set was made of aluminium, and this set was used when exciting the tube for a study of the green line radiation. These electrodes gave off considerable gas when operated over long periods and so our tubes were provided with a second set of electrodes made up of magnesium to clean up the gases released. It was generally a long process and it meant a tedious piece of work to clean up thoroughly these tubes for producing the green line radiation. Moreover it was not found practical to seal off the tubes from the pumps and the gas filling equipment.

In our latest experiments we have found that these green line radiation tubes can be made up quickly if care be taken to use tungsten electrodes and to thoroughly outgas these by raising them to incandescence, and, at the same time, to outgas the tubes as well by heating them to a high temperature for a time in an electric furnace. During this outgassing process the tube should be evacuated as highly as possible by the use of a mercury diffusion pump backed up by a pump of hyvac or other similar type, and at the same time by passing a weak discharge from a transformer through the residual gas, but not of sufficient strength to produce spluttering on the walls. With tubes made up in this way 30 cm. long and about 1.5 cm. in diameter green line radiation of strong intensity can be easily obtained. Moreover they can be sealed off from the pumps and the gas-filling equipment. It suffices to admit argon to the tube that has been most carefully and scrupulously purified by the passage of a current through it between calcium terminals and by making certain to dry the argon thoroughly. A small amount of oxygen thoroughly purified should then be added. We have made numerous experiments with varying amounts of argon mixed with oxygen in different proportions, and have found that we can get the best results when the argon is at a pressure of 3-4 mm. of mercury and the oxygen amounts to but a trace and is infinitesimal in amount. When a discharge is passing through the tube with argon alone in it the line λ 5577 does not appear in the spectrum at all, but when a

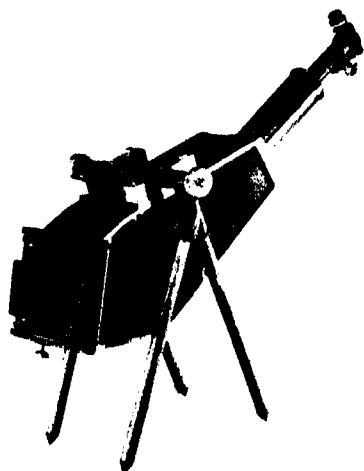


FIG. 1.

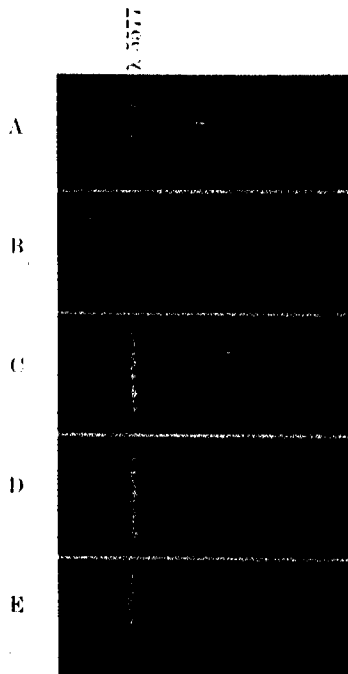


FIG. 5.—Spectrograms taken at Virginia Water, England; exposure C. taken between 1.45 and 2.45 a.m.

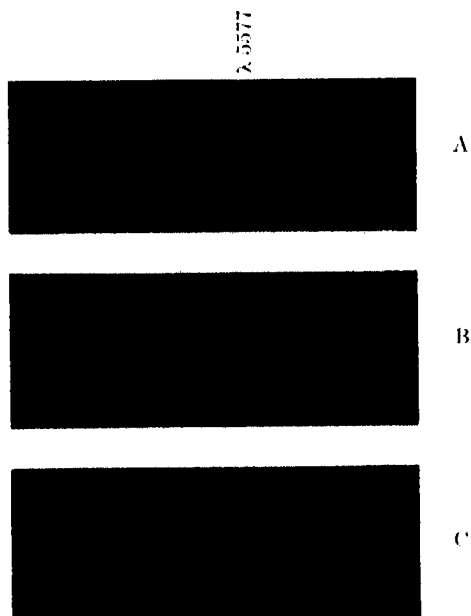


FIG. 4.—Spectrograms taken at Sulphur Mountain, Banff, Alberta, with exposures 10, 15 and 20 minutes.

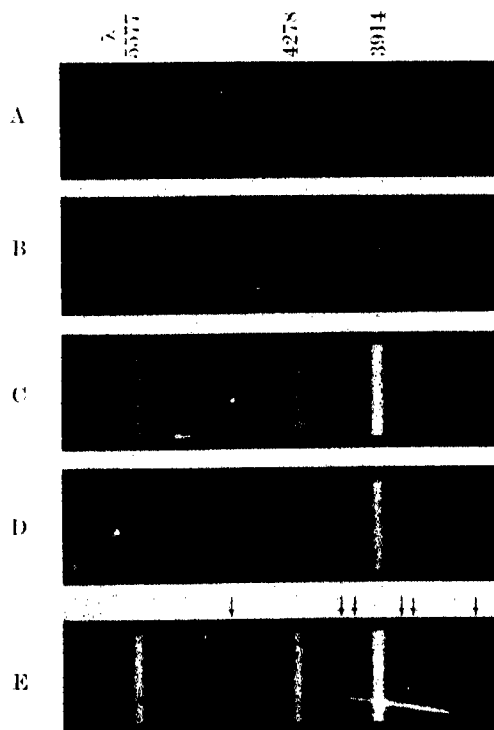


FIG. 6.

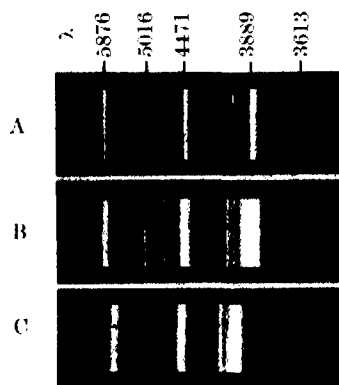


FIG. 7.— Helium Spectrum (Geissler).
A. Ross; B. Hilger; C. Mellish.

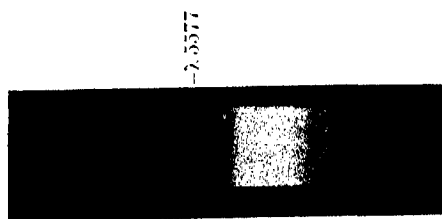


FIG. 8.



FIG. 9.

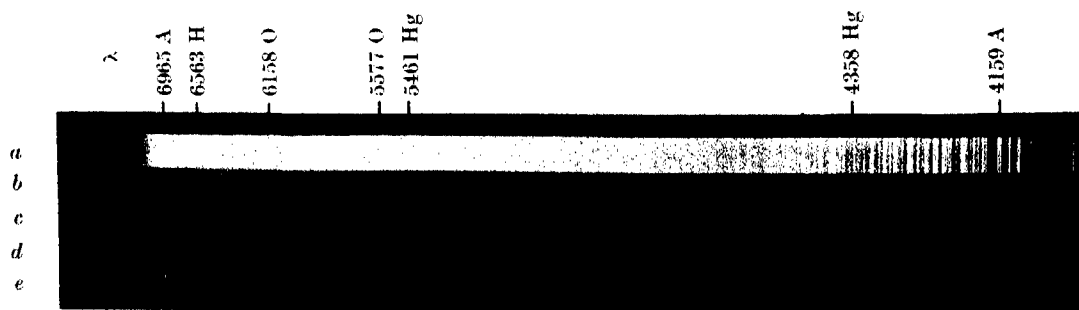


FIG. 10.

trace of oxygen is added the green line flashes out instantaneously with strong intensity.

In operating the tubes filled in this way the spectrum one ordinarily obtains consists of many lines belonging to the spectra of argon, oxygen and mercury. But when the tubes are in the condition we have just described and give spectra of this character we have found by reducing gradually the voltage applied to the tube and the current passing through it, that we can steadily weaken the intensities of all the lines in the spectrum until the only ones remaining visible are those corresponding to λ 6965 of the argon spectrum and λ 5577·341 of the oxygen spectrum. An example of such a residual spectrum is shown in (b) of fig. 10 (Plate 2). With the exception of the argon line λ 6965 this spectrum is practically a replica of the spectrum of the light of the non-polar aurora. It was taken with a Hilger constant deviation spectrograph and the plate used was of the Ilford Panchromatic Soft Gradation type. As to the spectra in fig. 10, (a) is an iron arc spectrum taken with an exposure of 25 seconds and (b) is the spectrum obtained with a green line tube discharge with an exposure of 1·5 hours. The mean potential applied to the tube was 500 volts and the current through it was too small to be read with a milliammeter. Spectrum (c) was obtained with 400 volts as a mean potential applied to the tube and the current while again too small to be read was greater than in case (b). The exposure was for 2 hours. For the spectrum (d) the exposure was also for 2 hours, the applied mean potential was 400 volts and the current was again greater but still less than could be read on a milliammeter. For (b) the current was probably of the order of a hundredth of a milliampere. The spectrum (e) was obtained from an argon filled Geissler discharge tube excited with a small transformer.

In this gradual weakening of the intensity of the lines in the spectrum obtained from the argon-oxygen mixture it was noted that the last lines to disappear prior to securing a spectrum with only the lines corresponding to λ 6965 of argon and λ 5577·341 of oxygen showing on the plate were λ 6459, λ 6158, λ 5331 and λ 4368 of the oxygen spectrum and λ 4159 of the argon spectrum. A reference to energy level tables for argon atoms shows that the excitation potential for λ 6965 is 13·47 volts and for λ 4159 it is 14·67 volts. By a reference to tables of energy levels for the oxygen atoms one finds that an excitation potential of 12·31 volts is required to bring out the wave-length λ 4368, one of 13·02 volts to bring out λ 5331, one of 12·7 volts to bring out λ 6158, and one of 12·6 volts to bring out λ 6459. It is known, too, that the dissociation energy of oxygen, 210 cal. is approximately the equivalent of a

7.0-volt excitation. This would, therefore, represent the energy of a neutral oxygen atom, *i.e.*, one in its normal or $^3P_2$ state. Immediately above the low $^3P_{012}$ states there is a metastable $^1D_2$ state with an energy equivalent of about 8.2 volts, *i.e.*, 1.2 volts higher than that of $^3P_2$. Above that again is the metastable $^1S_0$ state with an energy equivalent of 10.42 volts or 2.22 volts higher than that of the $^1D_2$ state. This difference of 2.22 volts is the equivalent of the auroral green line radiation with the wave-length λ 5577.341 and is determined by the fact that the auroral green line originates in the transition of oxygen atoms from the metastable $^1S_0$ energy state to the metastable $^1D_2$ one.

From a consideration of the spectra shown in "b" and "c," and of the energy equivalents of the spectral lines involved in them, a few conclusions can be drawn. In the first place the discharge in the tubes must have been mainly carried by the atoms of argon for the oxygen was present only in an infinitesimal amount. Since the line λ 6965 of argon was the only residual wave-length of this element remaining in spectrum (b) it follows that the mean potential available in the positive column when the discharge was passing was limited to 13.47 volts the excitation potential of λ 6965. It is known that argon atoms on emitting the wave-length λ 6965 revert to a metastable $^3P_2$ state with an energy equivalent of about 11.6 volts. These argon atoms in their metastable state would accumulate and would collide in time with the molecules of oxygen. In so doing they would pass on their energy of excitation to the latter. This could mean that the molecules of oxygen under this excitation would be dissociated and the resulting atoms left in the excited metastable states $^1S_0$ and $^1D_2$ or possibly in the $^1S_0$ and $^3P_2$ states. To accomplish this result an excitation potential of $10.5 + (8.3 - 7)$ or 11.8 volts would be approximately what was required. With the oxygen present in the discharge tube under great attenuation there would be a steady reversion of oxygen atoms in the $^1S_0$ metastable energy state to the $^1D_2$ one and this would account for the emission of the green line radiation of wave-length λ 5577.341. Moreover, collisions between atoms of argon in the excited metastable $^3P_2$ state with those of oxygen in the $^1D_2$ metastable energy state or the $^3P_2$ normal state could result in just sufficient energy being passed on to either the latter to leave them in the state to emit radiation having the wave-lengths $\lambda\lambda$ 6459, 6158, 5331 and 4368. This would account for the latter being penultimate wave-lengths when the excitation of the gas in the discharge tube was gradually lessened.

This explanation of the origin of the auroral green line radiation in these laboratory experiments is put forward tentatively. It would appear to be in

keeping with all the observed facts and it suggests that in seeking for the origin of the green line radiation from the moonless night sky we may find that molecules of nitrogen in an excited metastable energy state of approximately 10.5 to 11.8 volts play an important rôle.

We wish to acknowledge here our appreciation of a financial grant from the National Research Council of Canada to enable us to carry out a part of this investigation.

The Fine-Structure of Some Lines in the Visible Region of the Spectrum of Thallium III.

By J. C. McLENNAN, F.R.S., and ELIZABETH J. ALLIN.*

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From a study of the fine-structure of some lines in the arc spectrum of thallium Schüler and Brück† concluded that the nucleus of the thallium atom possessed a moment of momentum given by $\frac{1}{2}h/2\pi$ and this value was confirmed by work on the first spark spectrum‡ of the element. The value of the nuclear moment being known the structure of the lines in the second spark spectrum could be predicted and the present paper is the account of an investigation of a number of these lines which lie in the visible region, a comparison being drawn between the experimental and the theoretical results.

The source of light used was similar to the one employed by McLennan, McLay and Crawford in the excitation of the first and second spark spectra of thallium for the purpose of line classification. It consisted of a quartz tube about 50 cm. long and $1\frac{1}{2}$ cm. in diameter with a plain window in each end and provided with aluminium electrodes sealed into side tubes. The metal whose spectrum was to be studied was scattered along the bottom of the tube and the tube evacuated. The metal was then vaporised by heat supplied by a coil of nichrome wire wound on the tube. This coil must be wound non-inductively or the desired excitation will not be obtained. The high tension across the terminals was produced by joining them in series with the secondary of a 30,000-volt transformer and a spark gap of about 1 cm., a condenser being connected in parallel.

* Holder of a National Research Council of Canada Fellowship.

† 'Z. Physik,' vol. 55, p. 575 (1929).

‡ McLennan, McLay and Crawford, 'Proc. Roy. Soc.,' A, vol. 125, p. 570 (1929).

As in previous experiments* the light was analysed by means of a large glass transmission echelon grating. The light power of the optical system has, however, been greatly increased by substituting for the spectrograph formerly used a large constant deviation prism mounted directly behind the echelon, the camera lens and plate holder being supported from the same base.

Ilford "Special Rapid" panchromatic plates were used and exposures varied from 5 to 15 minutes.

The results obtained are tabulated below.

Table 1.

Unresolved line.			Fine-structure pattern.		
Wave-length. (Å.U.)	Intensity.	Classification.†	$\Delta\lambda$.	$\Delta\nu$.	Intensity.
6007.4	5	$7s^2S_{\frac{1}{2}} - 5d^9 6s 6p^2P^{\circ}_{\frac{1}{2}}$	0.538 0	-1.44 0	3 10
5499.4	2	$7p^2P^{\circ}_{\frac{1}{2}} - 6d^2D_{\frac{1}{2}}$	0.132 0	-0.438 0	5 10
5362.40	4	$7s^2S_{\frac{1}{2}} - 7p^2P^{\circ}_{\frac{1}{2}}$	0.107 0	-0.373 0	4 10
5086.99	4	$7p^2P^{\circ}_{\frac{1}{2}} - 8s^2S_{\frac{1}{2}}$	0.044 0 -0.112	-0.169 0 0.435	6 10 4
4891.8	8	$6p^2P^{\circ}_{\frac{1}{2}} - 5d^9 6s^2 2D_{\frac{1}{2}}$	0.289 0.123 0	-1.21 -0.514 0	6 10 6
4380.57	2	$7p^2P^{\circ}_{\frac{1}{2}} - 7d^2D_{\frac{1}{2}}$	0.082 0	-0.426 0	10 10
4269.81	6	$7p^2P^{\circ}_{\frac{1}{2}} - 7d^2D_{\frac{3}{2}}$	0 -0.078	0 0.428	10 5
4155.75	4	$5f^2F^{\circ}_{\frac{5}{2}} - 5g^2G^{\circ}_{\frac{3}{2}}$	0.038 0	-0.220 0	7 10
4109.85	7	$7s^2S_{\frac{1}{2}} - 7p^2P^{\circ}_{\frac{1}{2}}$	0 -0.157	0 0.029	10 10
3946.02	2	$7p^2P^{\circ}_{\frac{1}{2}} - 8s^2S_{\frac{1}{2}}$	0.095 0 -0.060	-0.609 0 0.378	10 10 5
3933.05	6	$5f^2F^{\circ}_{\frac{3}{2}} - 5g^2G$	0 -0.022 -0.133	0 0.145 0.860	8 10 2

† McLennan, McLay and Crawford, 'Proc. Roy. Soc.,' A, vol. 125, p. 50 (1929).

* 'Trans. Roy. Soc. Can.,' vol. 23, p. 7 (1929) and 'Phil. Mag.,' vol. 8, p. 515 (1929).

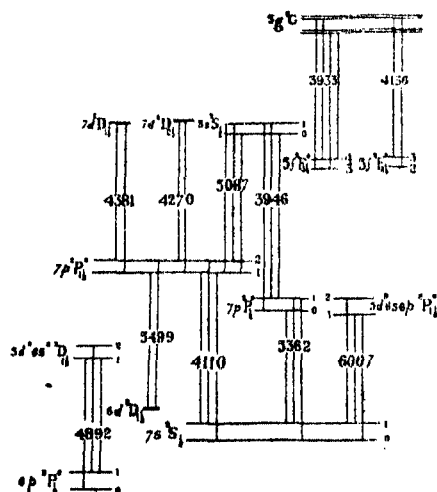
The intensities given for the components of the fine-structure patterns are not a measure of the true relative intensities of the lines but should be useful in indicating which components are strong and which very weak.

No values are given for the line $\lambda = 5927.8 \text{ \AA}$. another strong line in this region. The position of the satellite due to the $7p^2P_{11}^{\circ}$ separation would, using the value given by other lines for this term, fall in the same position as a second order of the line $\lambda = 5949$ of thallium II. It was impossible to tell from a study of the plates to which cause the line present in this position was due.

The value given by the line $\lambda = 3933 \text{ \AA.}$ for the term $5f^2F_{3/2}^{\circ}$ is subject to error since the two components overlap and that given for the line $\lambda = 4269.8 \text{ \AA.}$ is also uncertain due to overlapping with lines of carbon which were present in all the spectrograms.

The first and last of these difficulties could be overcome by a re-arrangement of the optical system in order to allow the light to pass through the prism before falling on the echelon. This may be done at a later date.

The figure gives the theoretical level scheme. It is not, of course, drawn to scale since it would, if this were done, be impossible to show the fine-structure separations on so small a diagram. The integers at the right-hand end of the



levels are the values of " f " and the number written across each group of lines is the wave-length of the unresolved line. The transitions indicated were all observed with the exception of the component of the line $\lambda = 5362 \text{ \AA}$. which corresponds to the transition* $f = 1$ to $f = 0$ and the component of the

* This symbol represents the resultant atomic moment of momentum in units of $\hbar/2\pi$.

line $\lambda = 4110 \text{ \AA}$. which corresponds to the transition $f = 1$ to $f = 1$. The missing line of $\lambda = 5362 \text{ \AA}$. may easily have been masked by the thallium arc line $\lambda = 5350 \text{ \AA}$. and in $\lambda = 4110 \text{ \AA}$. it is the weakest of the multiplet. In the case of the latter there is a third line present which would correspond to a satellite at $-0.071 \text{ \AA}$. but this is probably the mercury line $\lambda = 4108.07$.

From a study of this diagram and of Table I we arrive at the following values for the separations of the various terms.

Table II.

Term.	Separation.	Term.	Separation.
$6p \ ^2P_{1/2}^\circ$	1.21	$7d \ ^2D_{3/2}$	None observed
$6d \ ^2D_{1/2}$	Very small	$8s \ ^2S_{1/2}$	0.606
$7s \ ^2S_{1/2}$	1.37	$5d^2 \ 6s^2 \ ^2D_{1/2}^\circ$	0.699
$7p^2 \ ^3P_{1/2}^\circ$	0.375	$5d^2 \ 6s \ 6p \ ^2P_{1/2}^\circ$	1.44
$7p \ ^2P_{1/2}^\circ$	0.437	$5f \ ^2F_{3/2}^\circ$	0.145
$7d \ ^2D_{1/2}$	None observed	$5f \ ^2F_{2/2}^\circ$	0.220

In addition to these fine-structure separations that of the doublet term $^2G_{3/2, 1/2}$ is also observed. It is seen to have a value of 0.860 frequency units.

The reason why only two components were found for the line $\lambda = 6007 \text{ \AA}$. is now understood since we learn that the separations of the two levels involved in its production are very nearly the same. The relative intensity of the two components supports this explanation.

In no case was a measurement of the separation of the $^2D_{1/2}$ or $^2D_{3/2}$ terms possible. The components of the line $\lambda = 5499 \text{ \AA}$. were, however, obviously double and the relative intensity of the components of $\lambda = 4270 \text{ \AA}$. indicates the presence of both lines. The value of the separation of the term $7p \ ^2P_{1/2}$ given by the lines $\lambda = 4381 \text{ \AA}$. and $\lambda = 4270 \text{ \AA}$. is slightly lower than the value derived from other lines. This is to be expected since the strongest members of the group would, in each case, differ by an amount equal to the difference in the separations of the ^2D and $^2P_{1/2}^\circ$ terms.

Applying the formula* $a \sim Z_c z^2 / n_{eff}^3$. we should expect the magnitudes of the separations of the $7s \ ^2S_{1/2}$ and $8s \ ^2S_{1/2}$ terms to be in the inverse ratio of the cubes of their effective quantum numbers, i.e.,

$$\Delta \nu_{8s \ ^2S_{1/2}} / \Delta \nu_{7s \ ^2S_{1/2}} = 3.121^3 / 4.148^3 = 0.43.$$

Using the experimental results quoted above we have

$$\Delta \nu_{8s \ ^2S_{1/2}} / \Delta \nu_{7s \ ^2S_{1/2}} = 0.606 / 1.37 = 0.44.$$

* Goudsmit and Bacher, 'Phys. Rev.', vol. 34, p. 1503 (1929).

One might not expect such good agreement between the experimental and the theoretical ratios in the case of the terms $6p\ ^2P_{1/2}^\circ$ and $7p\ ^2P_{1/2}^\circ$ but actually it is quite as good.

Theoretically we have

$$\Delta\nu_{7p\ ^2P_{1/2}^\circ}/\Delta\nu_{6p\ ^2P_{1/2}^\circ} = 2.366^3/3.455^3 = 0.32,$$

and experimentally this

$$= 0.375/1.21 = 0.31.$$

We may also compare the separation 1.37 of the $7s\ ^2S_{1/2}$ level of thallium III with the separation 0.40 of the corresponding level in thallium I. This yields as the ratio $7s\ ^2S_{1/2}$ of Tl. I/ $7s\ ^2S_{1/2}$ of Tl. III the value 0.34.

$$n_{\text{eff.}}\ 7s\ ^2S_{1/2} \text{ of thallium III} = 3.12,$$

$$n_{\text{eff.}}\ 7s\ ^2S_{1/2} \text{ of thallium I} = 2.20,$$

therefore

$$\frac{(n_{\text{eff.}}\ 7s\ ^2S_{1/2} \text{ of Tl. III})^3}{(n_{\text{eff.}}\ 7s\ ^2S_{1/2} \text{ of Tl. I})^3} = 0.27.$$

In conclusion the authors wish to express their thanks to Dr. A. B. McLay and Mr. M. F. Crawford for the privilege of using results (at the time unpublished) obtained by them with a 3 m. concave grating and also for their interest and advice throughout the course of the investigation.

Zeeman Effects for Fine Structure Components of Thallium Spectral Lines.

By Prof. J. C. McLENNAN, F.R.S., and A. M. I. A. W. DURNFORD, M.A.*

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[PLATES 3-6.]

For many years the study of the Zeeman effect with various types of spectral lines has been a very successful method of investigating the electronic features of atomic structure. More recently it has proved to be a successful means of investigating some of the characteristics of atomic nuclei. Certain considerations now being brought forward, associate the fine structure of spectral lines with the spin of the nuclei of the atoms in which the radiation originates. As spectral lines with fine structure components having separations of a considerable magnitude have been found in the spectra of thallium and other elements, it is evident that in a study of the Zeeman effects for these components with magnetic fields of various strengths, a very promising field of investigation has been created.

In the investigation to be described in this paper our efforts were directed initially to securing Zeeman effects for certain prominent lines in the spark spectrum of thallium in order to obtain information which would lead to their correct classification. While this work was in progress, other investigators,† utilising the information at hand concerning the spectra of Hg I and Pb III, were able to assign classifications to a few of the wave-lengths of thallium II in question. These results are now embodied in the publication of a more extensive analysis by McLennan, McLay and Crawford (*loc. cit.*). It was thought well, however, to continue the Zeeman effect investigation having in mind either the confirmation of their classification or the extension of the information available regarding the Zeeman effect with elements of high atomic number. In general, the spectra of such atoms indicate interesting quantum vector coupling types.

The wave-lengths to which we gave special consideration at the commencement of our work were Tl $\lambda\lambda$ 5152, 5079, 4981 and 4737 A.U. It will be seen

* Holder of a Fellowship from the National Research Council of Canada (1928-29).

† Rao Narayan and Rao, 'Ind. S. Phys.' vol. 2, p. 467 (1928); McLennan, McLay and Crawford, 'Proc. Roy. Soc.,' A, vol. 125, p. 570 (1929).

that the last-mentioned wave-length has assigned to it, in the work of McLennan, McLay and Crawford, the classification $^1D_2 - ^1F_3^0$. The full notation is not used here, as no use is made of the orbital information in predicting the usual Zeeman effects. It follows from theories concerning the anomalous Zeeman effect that singlet to singlet transitions constitute the particular case of the anomalous Zeeman effect which leads to what has been called the normal Zeeman effect. Consequently in the line Tl λ 4737 we have a transition which, barring complications, should give a simple normal triplet. However, when Zeeman patterns were obtained, the distribution of the magnetically resolved components of the line Tl λ 4737 showed unsymmetrical characteristics. The predicted Zeeman effects for the remaining lines in question, although multi-component, would practically, on account of the unresolvable separation of components, give a triplet effect. Variations from this prediction were quite obvious in the case of Tl $\lambda\lambda$ 5079 and 4981. The experimental information possessed at this time strongly suggested that in the emission of radiation giving rise to thallium spark lines, complicating factors were involved that produced variations from the Zeeman effect one would predict by the application of ordinarily accepted rules.

In addition to the four wave-lengths mentioned above there exists in the thallium spark spectrum a very strong line at λ 5949 Å. This wave-length had been assigned the classification $^3S_1 - ^3P_2$ and therefore would have for its predicted Zeeman effect the pattern $\pm \frac{(0, 1) 2, 3, 4}{2}$. Such a type of Zeeman

pattern had been obtained already and showed distinct resolution in the case of the Zn line λ 4811. Accordingly, the investigation was extended to include the Tl line λ 5949 in an endeavour to ascertain the factors that were causing the Zeeman patterns of the Tl lines to have variations from their predicted types. The predicted Zeeman pattern for Tl λ 5949 is easily distinguished as there is a half normal separation between adjacent components and when the polarisations are separated there are three π components and six σ components. However, on obtaining a Zeeman pattern for Tl λ 5949 we observed five π components and five σ components, with indications that some of the components were composite. The Zeeman pattern as a whole differed widely from the predicted type.

The Zeeman effect of Tl λ 5949 was then obtained with different magnetic field strengths. The variation in the position of the components indicated a convergence to several distinct wave-lengths, and by ultimately employing a very weak field the Zeeman components were observed to converge to three

separate and sharp wave-lengths. This clearly showed that fine structure in the thallium spark lines was the factor that had caused the observed Zeeman patterns to deviate from the predicted types.

In taking spectrograms of the five strong lines in Tl II, mentioned above, we obtained other spark lines on the plates at the same time, and consequently included in our investigation the majority of the important lines in Tl II from the red to the ultra-violet and also the strongest Tl III lines. The classification of the latter is given in a communication of McLennan, McLay and Crawford.* The thallium arc line λ 3776 was resolved with a magnetic field different from any yet recorded and with the two polarisations separated. As this arc line possessed fine structure components, it has been included with the spark lines in this report of our work.

No attempt is made in the present communication to use the results as a test of the recent theories concerning the Zeeman effects of fine structure lines. The scope of the two sides of the subject is obviously too great to be included in a single paper, and accordingly the experimental side of the subject is presented as it appears to an unbiased observer. On account of the importance of the subject, considerable detail is employed in the presentation of the results, but it is hoped that any over emphasis in this regard will be atoned for by its usefulness to workers on the theoretical side of the subject.

Apparatus.

The apparatus used in the present investigation was the same as that used previously in studying "The Zeeman Effect for the Spectrum of Tantalum,"† with the exception that certain improvements in technique were introduced. These mainly consisted of the use of a Wollaston prism to separate the polarisations and the use of a detachable water-cooled negative electrode for carrying the thallium.

The first Wollaston prism employed gave a double image separation of 4 mm. at a distance of 100 mm. and had a circular aperture of 1 cm. diameter. This prism caused considerable loss in intensity requiring six times the exposure that was necessary when no prism was employed. A special prism was then obtained having the same double image separation but a circular aperture of 2.5 cm. diameter. Tests upon the latter prism indicated it to have five times the light power of the small aperture prism, and no appreciable loss in intensity resulted from its use. Its large aperture utilised the full aperture of the

* 'Proc. Roy. Soc.,' A, vol. 125, p. 50 (1929).

† McLennan and Durnford, 'Proc. Roy. Soc.,' A, vol. 120, p. 502 (1928).

quartz lens that brought the images to a focus on the slit of the grating spectrograph.

The Wollaston prism was employed in the optical train by placing it immediately in front of and on the source side of the focussing lens, the latter being 10 cm. from the source. The prism was held firmly in a brass fitting that was held tightly but capable of turning in a second fitting attached to the lens holder. The prism could thus be used in two positions, first, with the images separated in a vertical direction, and, secondly, with the images separated in a horizontal direction. As the slit of the spectrograph was vertical, the former position gave two images on the slit, having an angular separation sufficient to cause two completely separated images on the photographic plate. In this way it was possible to secure simultaneously a photograph of both polarisations.

The above procedure, however, was not always entirely satisfactory as the values of the separations had been calculated to comply with second order spectra. Thus when third order spectra were photographed the increased astigmatism caused an undesirable merging of the components, and consequently it was sometimes necessary to have both polarisations distinctly separated. This was most satisfactorily obtained by employing the Wollaston prism with the images separated in a horizontal direction and thus the image of only one polarisation fell on the slit. The latter effect was aided by the fact that the focussing lens gave a vertical line image of the point source. Ambiguous components of certain second order Zeeman patterns were definitely assigned to the correct polarisation by the means just cited.

In working with tantalum, only one detachable water-cooled electrode was used, the negative electrode being in the form of a tip in one of the pole caps. However, in working with thallium, as the metal is quite soft and unlike tantalum in many physical respects, a new method for handling the element had to be devised.

Pure thallium in the pole cap did not stand up against the shock of the vibrator, so that it was only natural to turn to the use of some alloy. As the use of zinc for field standards was desirable an alloy of zinc and thallium was at first employed, and it gave a very satisfactory combination as far as the above-mentioned difficulties were concerned. However, the spark lines required a longer exposure than one loading of the alloy would permit, and in consequence of this it was necessary to have a means of reloading the electrode with the element.

As the positive electrode was removable, the thallium was set in the copper

plate and a copper tip was used in the opposite pole cap. Pure thallium could be used in this arrangement and this method proved satisfactory enough to allow for an initial study of the Zeeman patterns desired.

In working with fields of the order of 1000 gauss and less it was found that the use of a Zn-Tl alloy in the vacuum arc had a very diminishing action on the intensity of the spark lines. This indicated the advisability of using pure thallium to obtain the thallium Zeeman effects and a separate zinc inset to obtain the standard patterns. In this way the standard patterns could be given any desired intensity independent of the length of exposure required for the thallium Zeeman patterns.

The amount of thallium that could be used in the copper plate of the positive electrode was limited to a cylinder of diameter 3 mm. and of length 1 mm. On account of the small area of thallium in contact with the copper plate, the cooling was very inefficient and renewals of thallium had to be made quite frequently. This method had the additional disadvantage that the last portion of thallium to burn away was directly against the mica strip and the heat caused by the arc invariably broke down the mica insulation. In consequence each renewal of thallium necessitated also a replacement of the mica strip.

In order to overcome these several disadvantages a different scheme of assembling the electrodes was devised. Figs. 1 to 4 "The Zeeman Effect for the Spectrum of Tantalum" (*loc. cit.*) illustrate the essential parts of the vacuum arc assembly. Fig. 1 of the present communication has been included to explain adequately the way in which the thallium was finally and most efficiently employed. Plate 3 shows the electrodes individually. The Zeeman effect apparatus with the various parts shown in their operating positions is clearly illustrated by Plate 6.

The positive electrode was fully insulated from its adjacent pole cap by means of a mica strip against the copper plate and a hard rubber ring surrounding the circumference of the pole cap. The outside diameter of the rubber ring was 15 mm. and the inside separation of the vertical copper tubes was 16 mm. This gave sufficient clearance to have the electrode swing flush against the pole cap. The mica strip and the copper plate each had a thickness of $\frac{1}{4}$ mm.

The negative electrode entered the discharge chamber through the side electrode outlet which was not used in the case of tantalum. By having the discharge chamber at the same electric potential as the negative electrode we did not require to insulate the negative electrode from the adjacent pole cap and the arc chamber.

The thallium was inserted in a hollow copper cylinder, 2 mm. in length, having an outside diameter of 4 mm. and an inside diameter of 3 mm. The copper cylinder was set in and soldered to a copper plate, $\frac{1}{2}$ mm. thick, the latter being soldered to a copper U-tube similar to that used for the positive electrode. In order to eliminate any up and down motion of the source, the inside separation of the copper tubing was made just greater than the diameter of the pole cap. The copper tubing passed out of the arc chamber through a cylindrical brass plug having on the outside two tapered hose connections. The inner end of the brass plug was a close fit in a hollow cylinder projecting 3 cm.

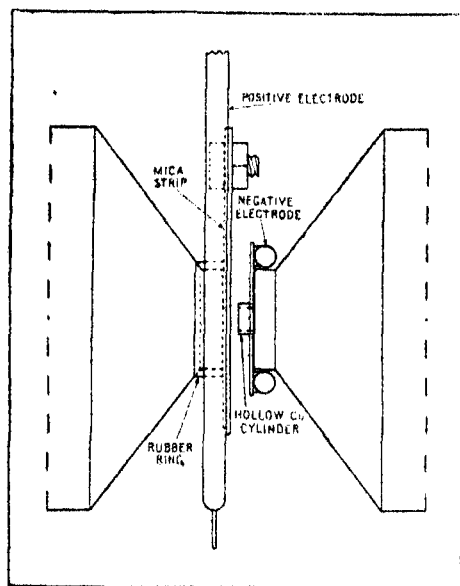


FIG. 1.—Electrode Assembly.

from the arc chamber, and having its outside diameter the same as the diameter of the outer end of the plug. A short length of thin-walled rubber hose furnished a vacuum-tight connection between the plug and the chamber.

To assemble the electrodes in the arc chamber it was necessary in the first place to insert the positive electrode and have it occupy the position shown in fig. 1. As the pole caps were separated by 4 mm. this left a 3-mm. gap, which was just sufficient to let the copper tubing of the negative electrode pass through. In constructing the negative electrode the bottom of the U was placed 2.5 cm. from the centre of the attached hollow cylinder, and 2.0 cm. from the nearest end of the copper plate. Thus the bottom of the copper U cleared the pole cap and snapped back into the position shown in fig. 1 before the copper

plate or cylinder was obstructed by the positive electrode. After the negative electrode assumed the position shown by fig. 1, there was a clearance of 1 mm. between the end of the hollow copper cylinder and the copper plate on the positive electrode, so that the negative electrode was simply pushed in to its operating position, where the hollow copper cylinder was at the centre of the pole cap.

The above method of assembling the electrodes thus utilised the 4 mm. pole gap in the following manner :—

- (a) Positive electrode— $\frac{1}{2}$ mm. mica, $\frac{1}{2}$ mm. copper plate.
- (b) Discharge gap—1 mm.
- (c) Negative electrode—copper cylinder with thallium, 2 mm. It will be seen that half the pole gap was devoted to the element whose spectrum was being studied.

The copper cylinder protected the thallium and maintained a concentrated discharge as the thallium burnt away. It had also the advantage that the whole supply of thallium could be utilised, and as this amounted to a cylinder 2 mm. long and of 3 mm. diameter we were able by using the method described to lengthen considerably the exposure obtainable from a single loading. As the copper plate on the positive electrode was not punctured under these conditions the mica lasted indefinitely and the copper plate outlived many thallium renewals. By having both electrodes removable, it is obvious that exposures of unlimited extent could be obtained in so far as the source was concerned.

The Zeeman patterns were obtained by the use of a concave grating with 50,000 lines (15,000 per inch), having a radius of curvature of 3 metres and employed in an Eagle mounting. The photographs taken were those of second and third order spectra. The light from the vacuum arc was focussed on the slit of the spectrograph by means of a quartz lens employing a sixfold magnification. The lens was rigidly attached to the spectrograph so that the magnet and vacuum arc assembly could be removed and replaced as desired.

Experimental Procedure.

Certain plates giving the π and σ components simultaneously but separate, showed a relative shift. This was quite noticeable for the ultra-violet wavelengths. Consequently it became necessary, in some cases, to secure one Zeeman pattern without the use of the Wollaston prism so that a relation between the positions of the π and σ components could be obtained.

Iford (10 inch by 2 inch) thin glass panchromatic plates gave very satisfactory results for all wave-lengths studied.

In order to have conditions as constant as possible exposures were taken during the night. By following this procedure we found that we greatly improved both the spectrographic and electrical conditions under which the work was done.

The current that passed through the windings of the electromagnet was maintained within 0.1 amp. of a fixed value by means of suitable outside resistances. For a current of 9.0 amp. and using the standard pole gap of 4 mm., the value of the field produced was 25,300 gauss. For a current of 5.0 amp. the value of the field was reduced to 23,000 gauss. Thus for either of these values a change of 2 per cent. in the magnet current would give an appreciably smaller change in the value of the magnetic field. In order to obtain the best resolution for the Zeeman patterns it was necessary to keep the source fixed in position and as localised as possible. The above conditions were very well satisfied by the method of electrode assembly illustrated in fig. 1.

The current used for the vacuum arc varied from 2 to 4 amp. As the thallium burnt away it was necessary to increase the current in order to keep a sufficient amount of thallium vaporised. This was obviously due to less efficient cooling of the thallium at the beginning.

The pressure in the vacuum arc chamber was maintained at a value between 1 and 10 mm. mercury. For this range of pressures the spectrum was observed to be entirely due to thallium, but if the pressure was allowed to increase above 10 mm. the copper spectrum became quite prominent. The latter was avoided as the Zeeman pattern of the Cu line λ 5153 interfered with that of the Tl line λ 5152.

In the case of thallium, exposures of 20-30 minutes' duration gave sufficient intensity for second order patterns. These exposures were frequently obtainable with one loading of the negative electrode. The zinc Zeeman patterns were easily obtained in 1 minute with an arc current of 2.5 amp. Weak third order patterns were obtained with net exposures of 80 minutes, but required overall exposures of nearly 4 hours.

The spectrum of the light emitted was kept under constant observation throughout the exposure. This was accomplished by using a hand spectroscope to view the light source through the second window of the vacuum arc chamber. This precaution ensured that consistent exposures were made. The use of the electromagnetic trembler described in "The Zeeman Effect

for the Spectrum of Tantalum" (*loc. cit.*) rendered the exposures practically continuous for each supply of the element.

Two second-order settings of the grating included all the wave-lengths that have been studied. Each setting covered approximately 650 A.U., the central wave-lengths for the two settings being λ 5945 and λ 4922. Ultra-violet lines were obtained as a result of overlapping third-order spectra. Since the two settings did not overlap, two sets of standard Zeeman patterns were used. For the higher setting the normal triplet of the Zn line λ 6362 was employed. Justification for taking the $2\delta\lambda$ separation of this triplet as a true measure of $2\delta\lambda_n$ has been discussed previously (*loc. cit.*). It was sometimes convenient to use the quartet and sextet patterns of the Na D lines for field references. Accordingly a comparison was made of their separations with those of the zinc triplet. For the lower setting the three zinc lines $\lambda\lambda$ 4811, 4722, 4680 furnished the required standard patterns. All three gave a value of the field in agreement to 0.1 per cent. and this value agreed with that obtained from the zinc triplet.

In order to obtain better resolution for the thallium lines $\lambda\lambda$ 5152 and 4737, third-order patterns were secured. Improvements were obtained in the case of λ 4737, but intensities were seriously affected as it required 10 times the exposure needed with second-order patterns. Third-order patterns were obtained for the three zinc lines mentioned above (figs. 27-29).*

Measurements of the separations of the components of the different Zeeman patterns were made directly upon the plates, by means of a Hilger comparator reading to 0.001 mm. Owing to the small value of the separations involved, a set of at least six readings was taken in each case, from which a mean value was secured. In the case of the standard patterns a set of 12 readings was taken. In general the latter showed only a variation of one in the last figure, the total separation being of the order of 0.5 mm. In applying the value of the field to the thallium measurements it was confined to three figures, as a variation of 0.5 per cent. in the field was present between measurements of different patterns on the same plate. This was due to a slight variation in the value of the field along the length of the pattern, and in the case of the weaker patterns, measurements were made at the position of greatest intensity.

The spectra of neon, the iron arc and the copper arc furnished an adequate range of wave-lengths from which dispersion data were obtained. A comparison of dispersion curves obtained from different plates that were secured

* The value of the magnetic field was calculated using the relation

$$H = 2.14 \times 10^4 \cdot \delta\lambda_n / \lambda^2 \text{ gauss.}$$

using the same setting of the grating indicated that a single dispersion curve was sufficiently accurate to be applied to all plates of a given setting. Consequently Dispersion/Wave-length curves were made for the various settings used and in converting the millimetre separations to Angstrom units the greatest possible error in the value of the dispersion employed was 0.1 per cent. The second-order dispersion varied from 2.58 (λ 6450) to 2.72 (λ 4550) A.U. per millimetre. For the third-order of λ 4740 the dispersion was 1.675 A.U. per millimetre.

Results.

The present Zeeman effect investigation embodies the examination of the magnetically resolved components from 18 wave-lengths of the various thallium spectra. These wave-lengths, together with their classifications and theoretical Zeeman effects (excluding fine structure), are given in Table I. In some

Table I.—Theoretical Zeeman Effects for Thallium.

λ .	Classification.	Zeeman effect.
6180	II $6s\ 7p\ ^3P^0_2$ — $6s\ 7d\ ^3D_3$	(0.00, 0.17, 0.33), 1.00, 1.17, 1.33, 1.50, 1.67.
5949	II $6s\ 7s\ ^3S_1$ — $6s\ 7p\ ^3P^0_2$	(0.00, 0.50), 1.00, 1.50, 2.00.
5928	III $7p\ ^3P^0_{1\frac{1}{2}}$ — $6d\ ^3D_{3\frac{1}{2}}$	(0.07, 0.20), 1.00, 1.13, 1.27, 1.40.
5828	II $6s\ 7s\ ^3S_1$ — $6s\ 7p\ ^1P^0_1$	(1.00), 1.00, 2.00.
5152	II $6s\ 6d\ ^3D_3$ — $6s\ 5f\ ^3F^0_4$	(0.00, 0.08, 0.17, 0.25), 1.00, 1.08, 1.17, 1.25, 1.33, 1.42, 1.50.
5079	II $6s\ 6d\ ^3D_3$ — $6s\ 5f\ ^3F^0_3$	(0.00, 0.08, 0.17), 0.92, 1.00, 1.08, 1.17, 1.25.
4981	II $6s\ 6d\ ^3D_1$ — $6s\ 5f\ ^3F^0_2$	(0.00, 0.17), 0.50, 0.67, 0.83.
4946	II	
4891	III	
4785	II $6s\ 7s\ ^3S_1$ — $6s\ 7p\ ^1P^0_1$	(0.00), 1.00.
4737	II $6s\ 6d\ ^1D_2$ — $6s\ 5f\ ^1F^0_3$	(0.33), 1.00, 1.67.
4110	III $7s\ ^3S_1$ — $7p\ ^3P^0_{1\frac{1}{2}}$	(0.13, 0.38, 0.64, 0.89), 0.25, 0.51, 0.76, 1.02, 1.27, 1.52, 1.78.
3933	III $5f\ ^3F^0_{3\frac{1}{2}}$ — $5g\ ^3G_4$	(0.02, 0.05, 0.08, 0.11), 1.00, 1.03, 1.06, 1.10, 1.13, 1.16, 1.19, 1.22.
	$5f\ ^3F^0_{3\frac{1}{2}}$ — $5g\ ^3G_5$	(0.67), 1.33.
3776	I $6p\ ^3P^0_{\frac{1}{2}}$ — $7s\ ^3S_1$	(0.03, 0.09, 0.14), 1.00, 1.06, 1.11, 1.17, 1.23, 1.28.
3456	III $6d\ ^3D_{2\frac{1}{2}}$ — $5f\ ^3F^0_{3\frac{1}{2}}$	(1.00), 1.00, 2.00.
3381	II $6s\ 6p\ ^1P^0_1$ — $6s\ 7s\ ^3S_1$	(0.03, 0.09), 0.77, 0.83, 0.89, 0.94.
3163	III $6d\ ^1D_1$ — $5f\ ^3F^0_{2\frac{1}{2}}$	(0.00), 1.00.
3091	II $6s\ 6p\ ^1P^0_1$ — $6s\ 7s\ ^1S_0$	

instances the classification is confined to the nature of the spectrum involved. The classifications presented are those assigned by McLennan, McLay and Crawford (*loc. cit.*). The theoretical Zeeman effects have been taken from tables compiled by Kiess and Meggers.* Table I thus furnishes a ready means

* 'Bur. Stds. J. Res.,' No. 23 (October, 1928).

of noting in the observed Zeeman patterns variations from the Zeeman effects predicted on the basis of no fine structure.

For the purpose of facilitating an interpretation of the results, diagrams depicting the Zeeman separations on an enlarged scale are included. Each component is designated by a letter so that various separations might easily be referred to. The diagrams are not intended to illustrate either the intensities or widths of the various components. In the case of Zeeman patterns with several components, intensities have been assigned taking the weakest component as unity. For this reason the values of the intensities for different lines and even different polarisations of the same line cannot be compared except in special instances. A general idea of the pattern in each case can be secured from the actual enlargement of the same.

Zeeman effect diagrams are not included for those patterns that are clearly given by the actual enlargement. The diagrams have been drawn on an arbitrary frequency scale, with the highest frequency component on the right. The enlarged Zeeman patterns give the components in the same manner, and for thallium the σ components are to be found at the top of each figure. Where more than two components are present in one polarisation, the positions of the various components are given on an arbitrary scale so that any desired separation can be determined. The π and σ components have been given the proper relative displacements. A correlation of diagrams, enlargements and measurements is made possible by specifying in the tables of results the actual measurements to which the figures refer.

The results have been grouped to bring together wave-lengths exhibiting similar resolutions in a magnetic field.

Table II, A, deals with two wave-lengths, each being produced as a result of a singlet to singlet transition. The predicted Zeeman effect is a normal triplet. It is to be noted that both wave-lengths give a departure from the predicted type but possess similar unsymmetrical Zeeman patterns. Fig. 2 (a) gives a diagrammatic representation of the pattern obtained for Tl λ 4737. Second-order patterns revealed a faint π component C, and indicated that the heavy π portion was double. This was confirmed by a third-order pattern. The σ components A and B were easily resolved, the mid-point of their positions being denoted by D. It is interesting to note that the σ DC separation is very nearly normal.

Fig. 2 (a) also serves to designate the components of Tl λ 3091. The π component C was not present and the π components A and B were not resolved. The σ components were similar to Tl λ 4737, A and B being clearly resolved.

Table II.

λ .	Field (kg.).	Separation.		$d\nu/d\nu_n$.	Figure.		
		Components.	cm. ⁻¹ .				
A.—Singlet to Singlet Transitions.							
4737	23.0	π A B	0.41*	0.38	2(a), 15.		
		π D C	1.24				
		σ D C	2.20				
	25.3	σ A B	0.77	1.04			
		σ B C	2.07				
		σ D C	2.45				
		σ A B	0.61*				
		σ B C	2.11*				
		σ D C	2.42*				
	3091	25.3	* σ A B	0.76		1.11	2(a), 19.
			σ B C	2.25			
			σ D C	2.63			
B.— ³ D — ³ F Transitions.							
5152	25.3	π doublet	0.31*	0.13	23.		
	23.0	σ 2 $d\nu$	2.36	1.10			
	25.3	σ 2 $d\nu$	2.59	1.10			
5079	23.0	π 2 $d\nu$	2.65	1.23	13.		
	25.3	π 2 $d\nu$	2.92	1.23	13.		
	23.0	σ 2 $d\nu$	2.79	1.30			
	25.3	σ 2 $d\nu$	2.92	1.24			
4981	23.0	π $d\nu$	1.49	0.80	14.		
	25.3	π $d\nu$	1.49				
	23.0	σ 2 $d\nu$	1.72		14.		
	25.3	σ 2 $d\nu$	1.89				

* Asterisk indicates measurements made from third-order patterns for λ greater than 4600 Å.U.

Table II, B, supplies the information obtained regarding the strong lines involved in the ³D³F multiplet. Tl λ 5152 was observed as a triplet and studied under two field strengths. The value of $d\nu/d\nu_n$ was found to be constant. The π component from a third-order pattern was observed to be double.

Tl λ 5079 shows considerable variation from the predicted type. The outer components of the π triplet gave a constant value for $d\nu/d\nu_n$. The central π component was relatively very intense and quite broad. The σ polarisation furnished a pseudo-quartet. Only the outer components could be measured, the inner set being rather diffuse. Indications that the

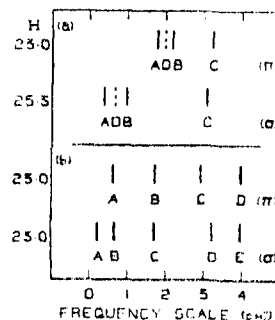


FIG. 2.—(a) Tl λ 4737 and λ 3091. (b) Tl λ 3776.

observed σ components were composite were evident from the fact that the outer components did not give a constant for $d\nu/d\nu_n$. Certain plates indicated the existence of a faint component outside and adjacent to the σ components measured.

The Zeeman pattern of Tl λ 4981 when obtained with considerable intensity revealed a faint π component associated with a very strong and broad π component. A 10 per cent. change in the field gave no relative displacement to the two components, their separation being 1.5 cm.^{-1} . The faint component observed in the Zeeman pattern had the higher frequency. The σ components of this pattern were not symmetrical, the higher frequency component of the doublet being 50 per cent. wider than the other. Nevertheless different field strengths gave a constant value for $d\nu/d\nu_n$.

Table III, A, deals with the wave-lengths which involve the $6s\ 7s\ ^3S_1$ term. Tl λ 4946 is included in this section, although its classification has not been established. The large Zeeman separations suggest, however, that it may probably be associated with the above term.

Table III.

λ .	Field (kg.).	Component.	Scale (cm. ⁻¹).	Intensity.	Figure.
A.—Transitions involving $6s\ 7s\ ^3S_1$.					
5949	21.4	π A	1.61	1	3, 6.
		π B C	4.63	10	
		π D	5.71	4	
		π E	6.59	4	
		σ A B	3.54	10	3, 11.
		σ C	4.83	4	
		σ D	5.56	10	
		σ E	7.42	4	
		σ F	8.17	1	
	23.0	π A	1.63		3, 26.
		π B	4.54		
		π C	4.86		
		π D	5.66		
		π E	6.60		3, 26.
		σ B	3.56		
		σ C	4.78		
		σ D	5.73		
	25.3	π A	1.73	1	3, 16.
		π B	4.57	9	
		π C	5.00	1	
		π D	5.65	4	
		π E	6.64	4	3, 17.
		σ A	3.22	4	
		σ B	3.58	5	
		σ C	4.70	4	
5828	No measurements.	σ D	5.79	9d	
		σ E	7.75	4	
		σ F	8.66	1	

Table III—(continued).

λ	Field (kg.).	Component.	Scale (cm. ⁻¹).	Intensity.	Figure.			
A.—(continued).								
4946	25.3	π A	3.73	2	4(a), 12.			
		π B	5.31	3d				
		π C	8.32	2				
		π D	10.00	2				
		σ A	4.71	3d				
		σ B	8.32	1				
4765	23.00	π A	3.86		4(b).			
		π B	5.40					
		π C	9.97					
		σ A	2.64					
		σ B	3.97					
		σ D	6.94					
	25.3	π A	3.81	2	4(b), 7.			
		π B	5.47	4				
		π C	10.00	3				
		σ A	2.42	3				
		σ B	3.81	3				
		σ C	5.18	1				
		σ D	7.00	7				
		σ E	8.29	1				
		σ F	9.78	2				
		σ G	11.53	2				
		3381	25.3	π A		3.00	2	4(c), 8.
				π B		7.76	3	
π C	10.00			2				
σ ?	0.05			1				
σ A	1.85			1				
σ B	4.64			1				
σ C	5.96			3				
σ D	9.30			1				
σ E	10.64			3				
d, diffuse component.								
B.—Thallium I.								
3776	23.0			π A	0.67	4	2(b), 10.	
		π B	1.76	10				
		π C	2.96	8				
		π D	4.00	5				
		σ A	0.27	4				
		σ B	0.69	4				
		σ C	1.74	1				
		σ D	3.24	6				
		σ E	4.00	5				
		25.3f	π A	0.51				
			π V	—				
			π C	2.93				
	π D		4.00					
	σ A		0.11					
	σ B		0.58					
	σ C		1.72					
	σ D		—					
	σ E		4.00					

f, from fourth-order pattern.

Table III—(continued).

λ	Field (kg.).	Component.	Scale (cm. ⁻¹).	Intensity.	Figure.
C.—Thallium III.					
5928		Triplet			
4891	25.3	π A	4.00	1	5(a), 9.
		π B	4.72	4	
		π C (?)	4.90	1	
		π D	5.36	1	
		σ A	3.60	4	
		σ B	4.00	4	
		σ C	4.92	1	
		σ D	5.63	6	
4110	21.4	π A	4.15	3	5(b).
		π B	4.66	3	
		π C	5.50	2	
		σ A	2.58		
		σ B	3.44		
		σ C	3.95		
		σ D	5.58		
		σ E	6.78		
	25.3	π A B	4.47	(2+4)	5(b), 18.
		π C	5.61	2	
		σ A	2.46	1	
		σ B	3.42	6	
		σ C	3.93	6	
		σ D	5.92	10	
3933		Triplet			
3456		Triplet			
3163		Triplet			

Tl λ 5949 was studied quite extensively. Zeeman patterns were obtained for five different fields. Patterns obtained with the polarisations together gave the relation of the π to the σ components (fig. 26, Plate 5). For a change of 15 per cent. in the value of the magnetic field, distinct differences were noted in the Zeeman patterns. The ultimate convergence of the Zeeman components was obtained with a field of the order of 1.0 kilogauss.

Fig. 3 illustrates the various changes which occurred in the Zeeman patterns as the result of employing different fields. The π component B occupied approximately the same position for all fields, and finally became the component B of the fine structure pattern. The π components A and C appeared to converge and shift to the left with decreasing fields ultimately occupying the position of the limit A (1.0 cm.⁻¹). For a field of 21.4 kg. the components

B and C merged. The π components D and E had separations proportional to the field and appeared to converge to the limit C (6.0 cm.^{-1}).

The σ components C and E resembled each other and had separations that were proportional to the several fields used. As the component C for decreasing fields moved to the right of the limit B (4.5 cm.^{-1}) it is evident that components C and E must be associated with the limit C (6.0 cm.^{-1}). For a field of 25.3 kg. components A and B were clearly separated and for a field of 21.4 kg. they merged. However, an intermediate field was useful in determining the convergence of the components. Thus for a field of 23.0 kg. the sharp component B came alongside the component A which had a fuzzy and diffuse appearance. Measurements showed that component B had moved to a lower

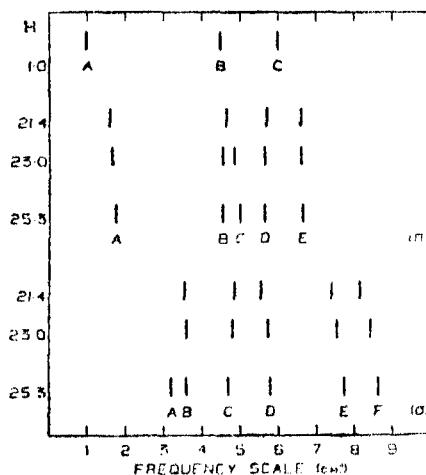


FIG. 3.—Tl λ 5949.

frequency position with the diminished field. This fact indicated that component B converged to the limit A (1.0 cm.^{-1}). The Zeeman member D for a field of 25.3 kg. had the same appearance as the combined components A and B in a field of 23.0 kg. In changing from a field of 25.3 kg. to 21.4 the intensity CG of the member D shifted from the low frequency side to the centre. Thus the member D is obviously composite and the sharp portion is probably the companion component of B. The fuzzy portion of D harmonised well with component A so that the latter two components appeared to us to be associated with the limit B (4.5 cm.^{-1}). The companion component of F if such exists might easily have been masked by the components A and B. The component F most probably converges to the limit C (6.0 cm.^{-1}).

Fig. 26 (Plate 5) illustrates the type of Zeeman pattern obtained for Tl λ 5949 with no distinction of the polarisations. The pattern included two sharp π and two sharp σ components, a feature which furnished an excellent means of securing the relative positions of the π and σ components when measured on plates with the polarisations separated. It also served to correlate the intensities of the components for different polarisations. At the same time, this type of pattern makes it quite obvious that without the use of the Wollaston prism one would have been seriously handicapped in making a correct analysis of the pattern.

In fig. 26 (Plate 5) the sharp σ component B can be seen superimposed on the fuzzy σ component A. A measurement of the position of B from this pattern yielded information that established the nature of the convergence of the σ components B and D.

Figs. 6 and 11 (Plate 4) show at the bottom the union of both polarisations. Increased intensity for this portion of the pattern served to locate some of the weaker components.

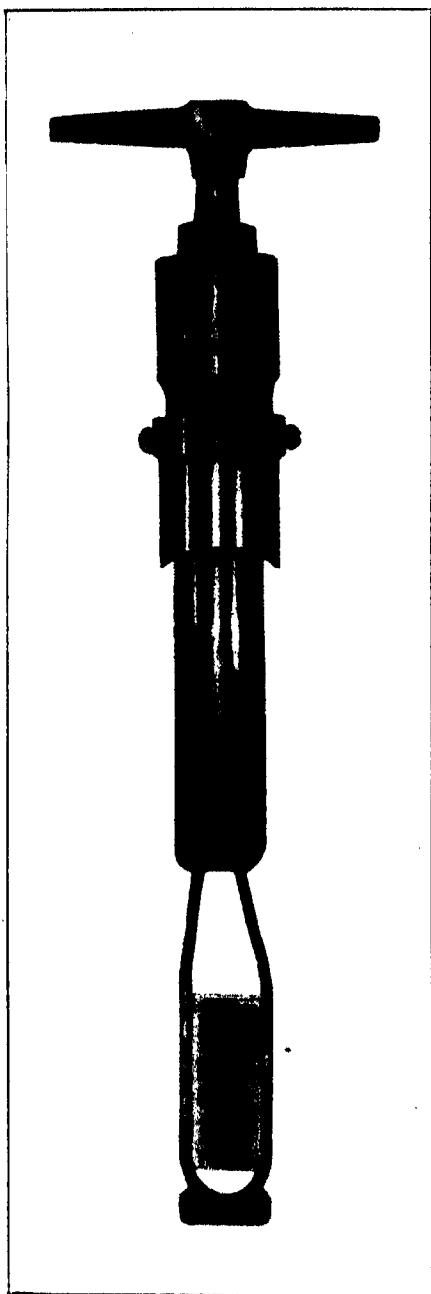
A measurable Zeeman pattern was not obtained for Tl λ 5828, but indications of a pattern with numerous components having a large overall separation were observed.

Fig. 4 (a) represents the separations obtained for Tl λ 4946. Four π components were observed, the member B appearing as a sharp component superimposed on a fuzzy one. Fig. 12 (Plate 4) illustrates this point and shows the two σ components fusing with the π . Plates giving the σ components alone revealed only the two components A and B.

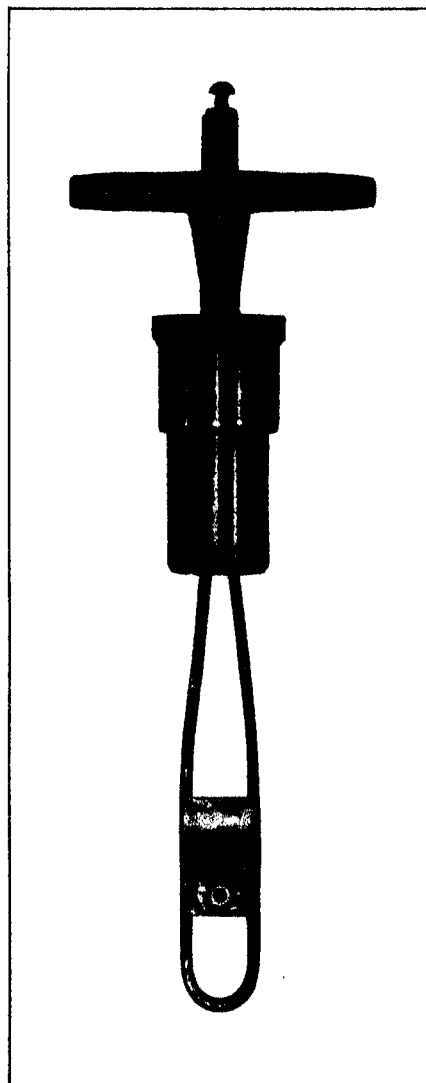
Tl λ 4765 was observed to give a many-component Zeeman pattern, and the stronger components were obtained for two field strengths. Fig. 4 (b) serves to designate the components and their separations. It will be noted that the π component C was little affected by the change of field whereas the separations of the components A and B were proportional to the field. The various components were quite sharp and distinct.

The Zeeman pattern for Tl λ 3381 was obtained with a field intensity of 25.3 kg. The π components were very sharp. It will be noted that the intervals are in the reverse order to Tl λ 4765. The σ components, B and D, were observed to be very close doublets. One plate indicated a component for the position 0.05 cm.^{-1} , having the same intensity as A, but as this component was not observed on other plates, which showed the component A, its existence is very doubtful.

Zeeman patterns for the line Tl λ 3776 were obtained from third- and



Positive Electrode.



Negative Electrode.

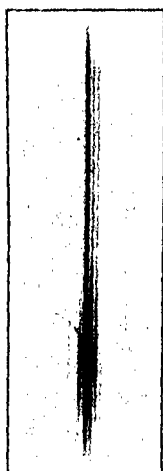


FIG. 6.
TI λ 5949

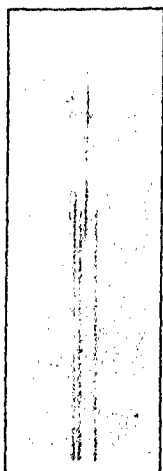


FIG. 7.
TI λ 4765

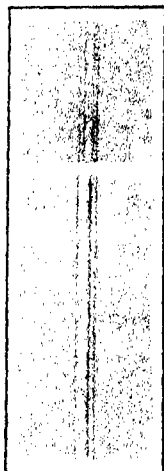


FIG. 8.
TI λ 3381

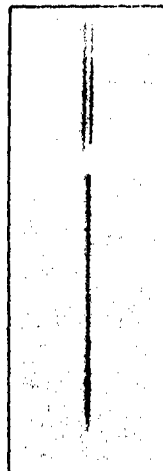


FIG. 9.
TI λ 4891



FIG. 10.
TI λ 3776



FIG. 11.
TI λ 5949



FIG. 12.
TI λ 4946



FIG. 13.
TI λ 5079

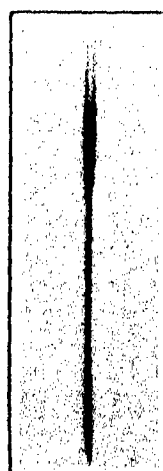


FIG. 14.
TI λ 4981

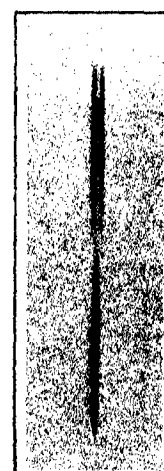


FIG. 15.
TI λ 4737

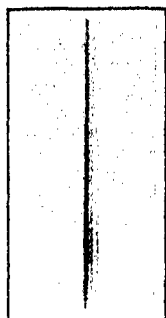


FIG. 16.
Tl λ 5949



FIG. 17.
Tl λ 5949

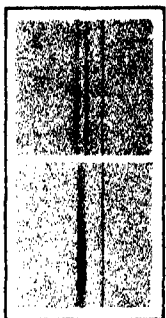


FIG. 18.
Tl λ 4110

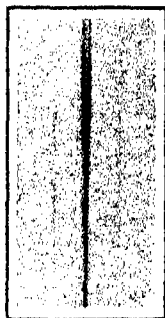


FIG. 19.
Tl λ 3091

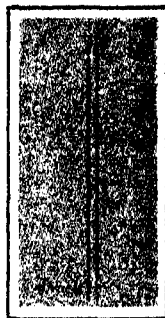


FIG. 20.
Tl λ 5949

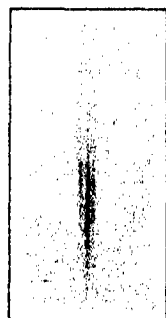


FIG. 21.
Tl λ 6180

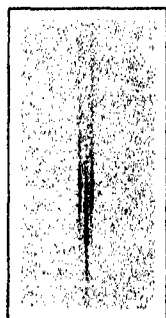


FIG. 22.
Tl λ 5928



FIG. 23.
Tl λ 5152



FIG. 24.
Tl λ 3933



FIG. 25.
Tl λ 3456

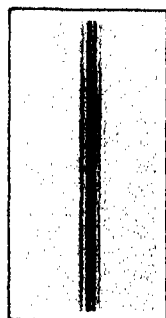


FIG. 26.
Tl λ 5949

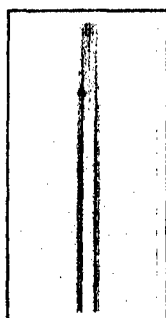


FIG. 27.
Zn λ 4811

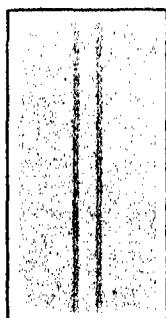


FIG. 28.
Zn λ 4722



FIG. 29.
Zn λ 4680

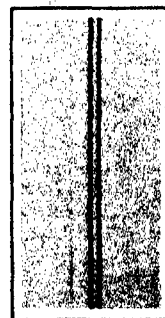
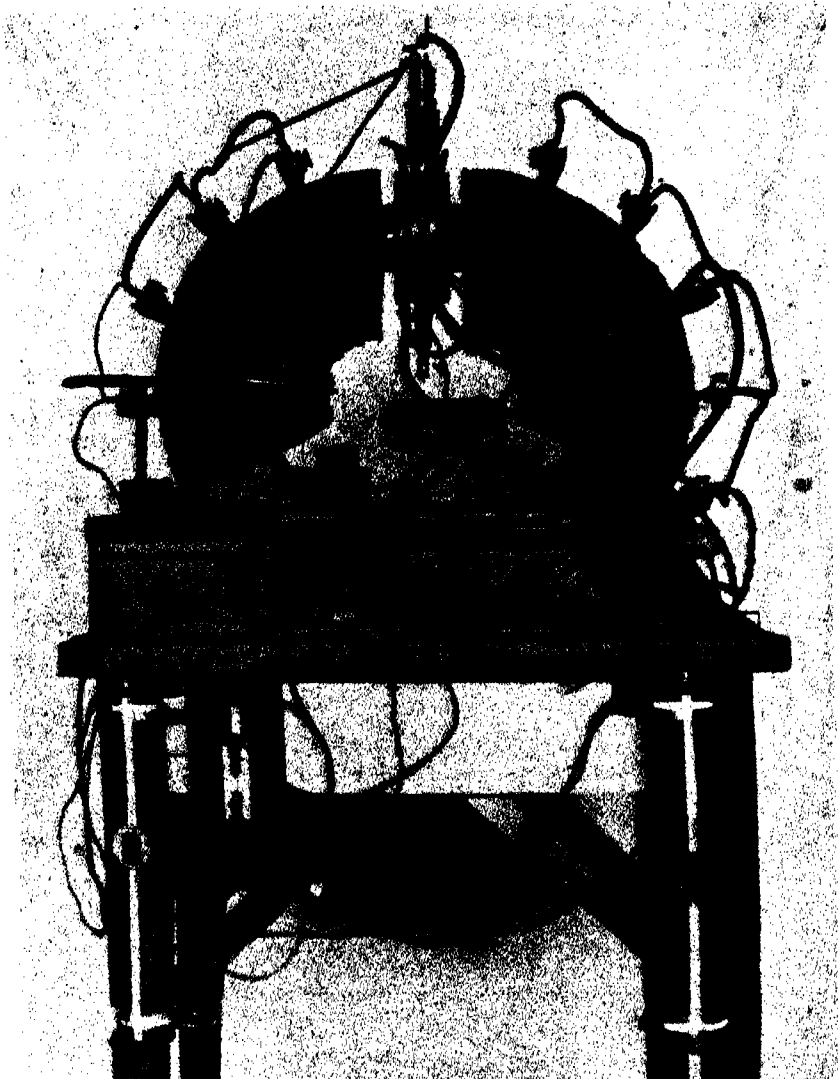


FIG. 30.
Tl λ 5949



Zeeman Effect Apparatus.

fourth-order spectra. Although the fourth-order pattern had a larger separation than the third, the components were more diffuse so that it supplied no additional information. Fig. 10 (Plate 4) is an enlargement of the third-order pattern and the separations can be obtained from Table III, B, supplemented by fig. 2 (b).

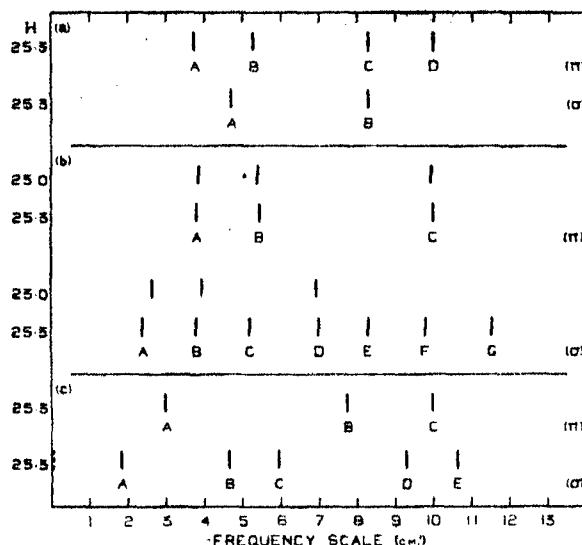


FIG. 4.—(a) Tl λ 4046. (b) Tl λ 4765. (c) Tl λ 3381.

Table III, C, deals with some of the Tl III lines that were studied. Two patterns require diagrams for the presentation of their separations. The others have been treated as triplets.

Of the above, fig. 5 (a), represents the pattern of Tl λ 4891. The π polarisa-

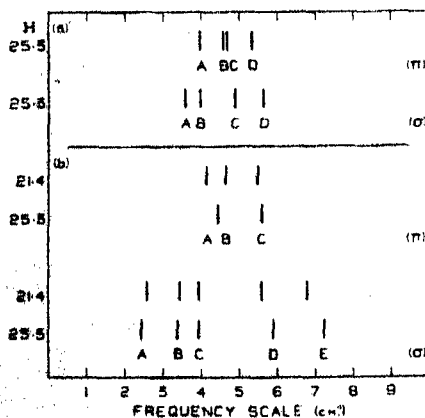


FIG. 5.—(a) Tl λ 4891. (b) Tl λ 4110.

tion furnished a pattern of a triplet nature. The outside components, however, were not equally displaced from the intermediate heavy component. Lack of clear resolution between B and D suggested a fourth member C on the right side of B. An estimated position for C is given in the table. The σ polarisation furnished four components. Components A and B were resolved on plates giving the sharpest lines.

Fig. 5 (b) designates the components of Tl λ 4110 as examined in two fields. The π components A and B were not resolved for a field of 25.3 kg. The intensity CG is noticeable at the high frequency side of the combined components. The behaviour of these components under various fields suggested that the member B was double, being broadened with increasing fields, component A being the companion of C. The positions of the various components were taken with respect to the Ne line λ 6163.6, which was present on the plates.

An examination of the σ polarisation suggested the presence of six components. The components A and E exhibited separations approximately proportional to the field. The behaviour of components B, C and D under the two fields indicated, strongly suggested that the component D was double and was made up of the companion components of B and C. The experimental behaviour supporting this statement is as follows. Components B and C were more clearly resolved for the stronger field but retained the same overall width for the two components. Component D appeared very sharp in a field of 25.3 kg., but the width of the line increased by 16 per cent. for the weaker field. If then the short frequency portion of D were the companion component of B, it would explain the displacements of the various components.

The remaining wave-lengths involved in the investigation included Tl II λ 6180 and several Tl III 'lines. Enlargements are given for all except Tl λ 3163, which was only obtained faintly. These lines gave Zeeman patterns which have been termed triplets. Values for the separations of the outer components of such triplets are given in Table IV. The pattern for Tl λ 3933 differed from others in that the π component was a diffuse band almost covering the region bounded by the outer σ components. It is quite probable that the other triplet effects represent unresolved multi-component Zeeman patterns.

Table V gives the normal Zeeman frequency separations for the values of the several fields employed. They were obtained by using the relation $d\nu_n (\text{cm.}^{-1}) = 4.674 \times 10^{-5} H$. As this relation is the exact complement of the one used for obtaining H it is evident that these normal separations are based directly upon the separations of the zinc Zeeman patterns.

Table IV.—Triplets.

λ .	Field (kg.).	$2 d\nu$ (cm. ⁻¹).	$d\nu/d\nu_n$.	Figure.
6180	21.4	2.16	1.08	21
5928	21.4	2.25	1.12	22
	25.0	2.60	1.11	
3933	25.0	2.55	1.09	24
3456	25.3	2.53	1.07	25
3163	25.3	2.25	0.95	

The spark lines vanished when the magnetic field was removed, thus indicating insufficient excitation with the vacuum arc alone. In an attempt to obtain the fine structure components of Tl λ 5949 a weak magnetic field was resorted to. It was found that reasonably sharp lines, with good intensity, could be consistently obtained. Decreasing the magnetic field had a very diminishing effect on the intensity so that the value ultimately used represented a compromise between intensity and sharpness.

Table V.—Normal Zeeman Separations.

H (kg.).	$d\nu_n$ (cm. ⁻¹).
25.3	1.182
25.0	1.168
23.0	1.075
21.4	1.000

Fig. 20 (Plate 5) illustrates the two strongest convergence limits for the Zeeman components of Tl λ 5949. These were obtained by the use of a magnetic field of the order of 1000 gauss. It will be noticed that they are very sharp. A preliminary examination of the Zeeman components for the purpose of determining their manner of convergence revealed that for a diminishing field the π component A experienced a divergence from the other components. This is clearly represented in fig. 3. This apparent anomaly suggested looking for a third convergence limit on the low frequency side of B (4.5 cm.⁻¹). In order to obtain sufficient intensity, the field was increased to about 4000 gauss. This procedure broadened the components but revealed the limit A (1.0 cm.⁻¹).

Fig. 30 (Plate 5) is an enlargement of the convergence pattern obtained in the latter manner. Measurements of this convergence pattern were taken

by McLennan, McLay and Crawford (*loc. cit.*) to represent the fine structure components of the line. Subsequent exposures gave the lines with less broadening. Measurements of the separations have been taken from several plates and it is interesting to note the constancy of the same, in spite of the fact that the magnetic fields differed from 4 to 1 kg. The results of this examination are given in Table VI. The Ne wave-length referred to is λ 5944.834 A.U.

Table VI.—Convergence Limits for Zeeman Components of
Tl λ 5949.

A.

Separation	Ne — C	C — B	B — A
Independent observations	4	7	4
Mean value (A.U.)	4.062	0.528	1.235
Average deviation (A.U.)	0.008	0.004	0.002
Mean value (cm. ⁻¹)	—	1.49	3.49

B.

Limit.	λ (A.U.).	Frequency scale.	Intensity.
A	5950.66	1.00	1
B	5949.42	4.49	10
C	5948.90	5.98	5

The above results have been given in frequency units in order that any desired separation of components can be conveniently expressed in terms of the normal Zeeman separation. The same is also desirable for application to fine structure analysis. The results have been derived from consistent sets of values, which have been supported by measurements from several independent plates. The consistency in the case of measurements of the field standards has been shown previously. For sharp components (*e.g.*, σ components C and E, π components A, D and E, figs. 3, 16 and 17) it was possible to obtain a set of values having agreement to within 0.001 mm., which was the limit imposed by the comparator. For fuzzy components having a sharp intensity centre of gravity the same degree of consistency was obtainable, measurements being taken upon the C.G. For extreme cases, where the component was broad and showed no intensity peak, measurements were taken upon the sides, and the mean of these measurements is then given as the position of the component.

A $d\lambda$ separation of 1 A.U. = 4 cm.⁻¹ for λ 5000 and approximately 6 cm.⁻¹

for λ 4000. Zeeman patterns for wave-lengths less than 4600 were obtained from overlapping third-order spectra so that the increased dispersion just compensated for the higher frequency associated with the smaller wave-length. Thus, an error of 0.001 mm. in the measurement secured from the plate amounted to an error of approximately 0.01 cm.^{-1} for both λ 5000 and 4000. The frequency results have been calculated using three decimal places with the tables giving the positions of the components to the nearest second decimal figure.

Conclusion.

It has been shown by Back and Goudsmit*† that the introduction of a new quantum number I, together with the quantum numbers S, L, and J, which are associated with the resultant spin moment, resultant orbital moment and total moment of the electrons respectively, served to account for the existence of fine structure in spectral lines. Experimental work connected with the spectra of Tl (*loc. cit.*) supports the conception that I is intrinsically associated with the nucleus as a spin moment.

Back and Goudsmit (*loc. cit.*) suggested that for what might be considered a relatively strong field (Paschen-Back effect) the fine structure terms would be divided into $(2I + 1)$ levels. The observed Zeeman effect would then be composed of groups of $(2I + 1)$ components, one group being associated with each Zeeman component that would have been observed had no fine structure been present. The finding of groups of 10 components in the case of Bi λ 4722 accordingly yielded the value $4\frac{1}{2}$ for the nuclear spin moment.

The Zeeman effect for Tl λ 3776 was given by Back in 1923.‡ More recently, Goudsmit and Bacher§ have considered the magnetic resolutions for a field of 43,350 gauss, which they describe as producing a "not yet complete" Paschen-Back effect. Information regarding the Zeeman pattern for weaker fields is given in the present communication.

In view of the fact that the field required to cause a Paschen-Back effect is dependent upon the magnitude of the fine structure term separations, the values of the magnetic fields employed in the present investigation were not sufficient in the cases we observed to produce the predicted doubling of components. The pattern obtained for Tl λ 4737 is suggestive of an incomplete Paschen-Back effect.

* 'Z. Physik,' vol. 43, p. 321 (1927); 'Z. Physik,' vol. 47, p. 174 (1928).

† Schüller and Bruck, 'Z. Physik,' vol. 55, p. 575 (1929).

‡ 'Ann. Physik,' vol. 70, p. 333 (1923).

§ 'Phys. Rev.,' vol. 34, p. 1499 (1929).

The quantitative measurements we have made on the magnetic resolutions given by the four wave-lengths involving the $6s\ 7s\ ^3S_1$ term of Tl II should be of considerable value in deducing the g values and the magnetic energy levels associated with that term.

The authors wish to express their appreciation of the interest and valuable suggestions contributed to the investigation by Dr. A. B. McLay.

Relative Intensities of Stark Components in Helium.

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(Communicated by A. S. Eve, F.R.S.—Received May 2, 1930.)

[PLATES 7, 8.]

Introduction.

Theoretical values for the displacements and relative intensities of Stark components have been calculated by Foster* for selected groups of helium lines. These were based on approximate methods in the perturbation theory of quantum mechanics, and on the assumption that the source contains equal numbers of atoms excited to states with a common principal quantum number.

Experimental work on this subject has been carried out by Foster, Takamine and Werner, and more extensively by Dewey.† The observed displacements agree remarkably well with the theory; but the intensities have shown some variations which cannot be disregarded. This appears surprising at first sight, since the theory reveals close connections between displacements and intensities. It seems, however, well established by Dewey that the $P - P$ (and $p - p$) combination lines are decidedly too strong for the theory. There appear to be other less striking discrepancies.

In the above experiments, the fields were rather low so that the individual Stark components in the visible spectrum were for the most part unresolved. The use of low fields may contribute appreciably to the error in the results,

* 'Proc. Roy. Soc.,' A, vol. 117, p. 137 (1927).

† Foster, 'Phys. Rev.,' vol. 20, p. 214 (1922); Takamine and Werner, 'Naturwiss.,' vol. 14, p. 348 (1925); Dewey, 'Phys. Rev.,' vol. 28, p. 1108 (1926), and vol. 30, p. 770 (1927).

since in that region especially the intensities of many lines show a very rapid variation with field strength. Moreover, so long as the components remain unresolved, one cannot know whether disagreement with theory is limited to some components in particular, or is general.

By employing somewhat higher fields and comparatively high dispersion, the writer has been able to investigate quantitatively intensity relations in the fine analysis of the Stark effect in helium. Since most of the individual Stark components are resolved there is a greater opportunity to make comparisons with theory.

These are made more accurate by the fact that the theoretical intensities are more "stable" in high fields (fig. 1). A new modification of the Lo Surdo source offers a further advantage in the production of Stark components which branch out from the main line until they reach maximum field and then run parallel for an appreciable distance (Plates 7, 8). In the latter region the intensities may be measured with some precision. The measurements are carried out through a variation of the general photographic-photometric method described by Dorgelo.*

The lines investigated include the parhelium groups $2P - 4Q$ (λ 4922) and $2P - 5Q$ (λ 4388) and the orthohelium groups $2p - 4q$ (λ 4471) and $2p - 5q$ (λ 4026).

For the most part there is detailed agreement with the theory (fig. 3). Definite variations do appear, however, in a few lines or components. The $P - P$ and $(p - p)$ combination lines, for example, are decidedly stronger than theory predicts. This is believed to result from the relatively large numbers of atoms excited to the P (and p) states.

Theoretical Calculations.

Foster has given the details of the method of calculating the relative intensities of the components of a line group. The treatment is an application of matrix mechanics to the perturbed helium atom considered as a doubly perturbed hydrogen system.

The theoretical relative intensities for the components observed by the writer are given in Table I. The values at field strengths of 10, 40, and 100 kilovolts per centimetre are due to Foster.

The method of calculation is approximate, and depends upon the introduction of the observed "hydrogen differences" of the helium terms. The accuracy of the calculated values is limited by these factors.

* 'Phy. Z.', vol. 26, p. 756 (1925).

Table I.
2P — 4Q (λ 4922).

Field in kv./cm.	Change in m .	Parallel components.			Perpendicular components.		
		D.	F.	P.	D.	F.	P.
10	2-1 1-1, 1-0 0-0, 0-1	—	—	—	0.52	0.079	—
		0.50	0.098	0.0034	0.25	0.049	0.0017
		0.33	0.069	0.0038	0.082	0.017	0.0009
20	2-1 1-1, 1-0 0-0, 0-1	—	—	—	0.440	0.155	—
		0.430	0.145	0.0205	0.215	0.0730	0.0100
		0.385	0.0985	0.0140	0.0715	0.0245	0.0035
30	2-1 1-1, 1-0 0-0, 0-1	—	—	—	0.405	0.200	—
		0.400	0.160	0.0350	0.200	0.0810	0.0175
		0.270	0.105	0.0265	0.0670	0.0260	0.0066
40	2-1 1-1, 1-0 0-0, 0-1	—	—	—	0.38	0.22	—
		0.39	0.15	0.059	0.19	0.077	0.029
		0.26	0.094	0.047	0.065	0.024	0.012
60	2-1 1-1, 1-0 0-0, 0-1	—	—	—	0.355	0.245	—
		0.370	0.120	0.105	0.185	0.0610	0.0540
		0.250	0.0740	0.0765	0.0620	0.0185	0.0190
100	2-1 1-1, 1-0 0-0, 0-1	—	—	—	0.33	0.27	—
		0.35	0.068	0.18	0.18	0.034	0.090
		0.24	0.045	0.12	0.059	0.011	0.029

Table I—(continued).
2P — 5Q (λ 4388).

Field in kv./cm.	Change in m .	Parallel components.				Perpendicular components.			
		D.	F.	G.	P.	D.	F.	G.	P.
10	2-1 1-1, 1-0 0-0, 0-1	—	—	—	—	0.28	0.22	0.099	—
		0.31	0.17	0.079	0.042	0.155	0.066	0.040	0.021
		0.21	0.11	0.049	0.034	0.052	0.027	0.012	0.0090
20	2-1 1-1, 1-0 0-0, 0-1	—	—	—	—	0.225	0.245	0.135	—
		0.280	0.160	0.0395	0.120	0.140	0.080	0.0195	0.0610
		0.195	0.105	0.0230	0.085	0.0480	0.0260	0.0055	0.0215
30	2-1 1-1, 1-0 0-0, 0-1	—	—	—	—	0.205	0.250	0.140	—
		0.275	0.140	0.0096	0.180	0.135	0.0690	0.0048	0.090
		0.190	0.0900	0.0090	0.120	0.0470	0.0225	0.0023	0.0300
40	2-1 1-1, 1-0 0-0, 0-1	—	—	—	—	0.20	0.25	0.15	—
		0.27	0.12	0.0008	0.21	0.13	0.060	0.0004	0.10
		0.185	0.077	0.0025	0.135	0.046	0.019	0.0006	0.034
60	2-1 1-1, 1-0 0-0, 0-1	—	—	—	—	0.190	0.250	0.155	—
		0.265	0.0990	0.0003	0.230	0.135	0.0495	0.0001	0.115
		0.180	0.0720	0.0000	0.145	0.0450	0.0180	0.0000	0.0365
100	2-1 1-1, 1-0 0-0, 0-1	—	—	—	—	0.18	0.25	0.16	—
		0.26	0.080	0.014	0.25	0.13	0.039	0.0070	0.12
		0.17	0.070	0.0000	0.15	0.043	0.017	0.0000	0.038

Table I—(continued).
 $2p - 4q$ (λ 4471).

Field in kv./cm.	Change in m.	Parallel components.		Perpendicular components.	
		<i>d.</i>	<i>f.</i>	<i>d.</i>	<i>f.</i>
10	2-1	—	—	0.55	0.50
	1-1, 1-0	0.53	0.071	0.26	0.036
	0-0, 0-1	0.35	0.051	0.087	0.013
20	2-1	—	—	0.470	0.120
	1-1, 1-0	0.450	0.150	0.225	0.0750
	0-0, 0-1	0.295	0.105	0.0735	0.0265
30	2-1	—	—	0.435	0.165
	1-1, 1-0	0.405	0.195	0.200	0.0970
	0-0, 0-1	0.265	0.135	0.0860	0.0340
40	2-1	—	—	0.405	0.19
	1-1, 1-0	0.37	0.22	0.19	0.11
	0-0, 0-1	0.24	0.15	0.061	0.039
60	2-1	—	—	0.360	0.225
	1-1, 1-0	0.335	0.260	0.170	0.130
	0-0, 0-1	0.220	0.175	0.0545	0.0440
100	2-1	—	—	0.335	0.255
	1-1, 1-0	0.29	0.29	0.15	0.14
	0-0, 0-1	0.19	0.20	0.047	0.049

Table I—(continued).
 $2p - 5q$ (λ 4026).

Field in kv./cm.	Change in m.	Parallel components.				Perpendicular components.			
		p.	d.	f.	g.	p.	d.	f.	g.
10	2-1	—	—	—	—	—	0.32	0.20	0.080
	1-1, 1-0	0.0017	0.29	0.20	0.11	0.0008	0.14	0.099	0.067
	0-0, 0-1	0.0017	0.19	0.13	0.081	0.0004	0.047	0.032	0.020
20	2-1	—	—	—	—	—	0.250	0.230	0.115
	1-1, 1-0	0.120	0.230	0.220	0.160	0.0059	0.115	0.110	0.0790
	0-0, 0-1	0.0070	0.150	0.140	0.110	0.0018	0.0370	0.0365	0.0280
30	2-1	—	—	—	—	—	0.220	0.250	0.135
	1-1, 1-0	0.0205	0.185	0.235	0.180	0.0105	0.0930	0.115	0.0890
	0-0, 0-1	0.0150	0.120	0.150	0.120	0.0038	0.0285	0.0380	0.0300
40	2-1	—	—	—	—	—	0.20	0.25	0.14
	1-1, 1-0	0.030	0.16	0.22	0.19	0.015	0.082	0.11	0.10
	0-0, 0-1	0.026	0.10	0.14	0.13	0.0064	0.025	0.034	0.033
60	2-1	—	—	—	—	—	0.185	0.255	0.150
	1-1, 1-0	0.0630	0.125	0.205	0.210	0.0315	0.0630	0.105	0.105
	0-0, 0-1	0.0470	0.0720	0.125	0.145	0.0115	0.0180	0.0310	0.0360
100	2-1	—	—	—	—	—	0.18	0.26	0.16
	1-1, 1-0	0.13	0.060	0.18	0.23	0.063	0.030	0.093	0.12
	0-0, 0-1	0.11	0.020	0.10	0.16	0.027	0.0054	0.026	0.041

A plot of the intensity-field relations brings out more clearly the importance of working at high electric fields. In fig. 1 the curves for the parhelium groups $2P - 4Q$ and $2P - 5Q$ are given. The letters refer to the k values and the numbers to the m values of the *initial* state, where the observed energy change is effected. The components corresponding to an m value change $0 \rightarrow 1$ have not been represented, since they are very weak, cause confusion in the graph and add nothing to its usefulness.

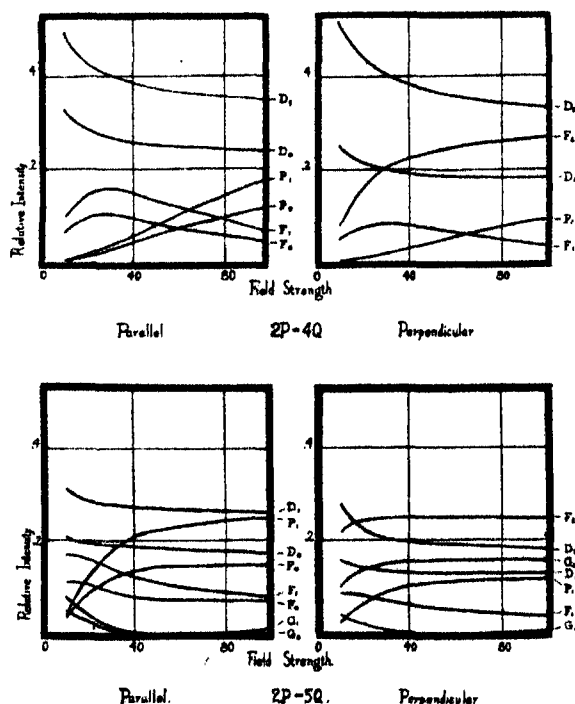


FIG. 1.—Theoretical Intensity-Field Relations.

It will be noted that the relative intensities of the components tend to reach certain limiting values as the disturbance due to the external field becomes comparable to that of the perturbing central field. As might be expected, these values are reached at much lower fields in the $2P - 5Q$ group than in the $2P - 4Q$ group. The curves for the orthohelium groups $2p - 4q$ and $2p - 5q$ show the same general characteristics.

The rapid variations in the relative intensities of the components at low fields is very striking. In addition, the displacements from which the field strength is determined are small. In view of these facts the precision of comparisons of theory and experiment is very much favoured with fields above

30 or 40 kilovolts per centimetre. It is felt that this is an essential point in the experimental procedure.

Experimental.

The source used in this research was a special type of Lo Surdo tube which the author has developed for intensity work. The precision of intensity measurements of this type depends to a great extent on the precision of the photometric process. It is therefore essential that the Stark components run parallel at maximum field for an appreciable distance. Such a field distribution was obtained by suitably shaping the walls confining the discharge near the cathode (see Plates 7, 8).

The cathode section of the tube is shown in fig. 2. The shape and dimensions of the hole in the lavite, and the distance of the cathode surface from the lavite shoulder, were the important factors in obtaining this field distribution. The correct position of the aluminium cathode, which is a very critical thing, was found by taking trial plates before each run, with a very wide slit and short exposure time.

These tubes were operated at a pressure of from 1 to 3 millimetres of mercury. The terminal voltage was in the region of from 8 to 10 kilovolts, with a current of from 1 to 6 milliamperes. Exposure times varied from 15 minutes for the most intense group to 2 hours for the weakest group. The life of a tube was in general about 3 hours.

The source of potential from which these tubes were operated was a split transformer rectifier* capable of supplying 100 milliamperes at 10,000 volts. An electrostatic voltmeter provided a means of determining terminal voltage.

The vacuum system was of large volume to lessen pressure effects, and the helium was purified by passing it over charcoal at liquid air temperature.

The light from the source was passed through a lens and Wollaston prism, and the two resulting polarised images were focused on the slit of the spectrograph with a magnification of about two. The light polarised with its electric vector parallel to the field of the source was passed through a quartz plate to reduce loss of light by reflection from the prism faces.

The large six prism glass spectrograph used in this work has been described elsewhere.† The prism chamber was kept slightly above room temperature

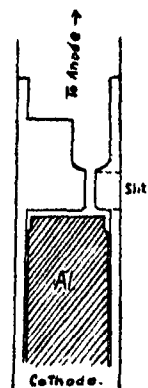


FIG. 2.

* Foster, 'Proc. Roy. Soc.,' A, vol. 114, p. 47 (1927).

† Foster, 'Proc. Roy. Soc.,' A, vol. 122, p. 599 (1929).

by a thermostat, since small temperature variations were found to materially affect the resolution of the instrument. Its dispersion was :—

λ (Å)	4026	4388	4472	4922
Dispersion (Å/mm.)	2.22	3.95	4.17	5.34

Eastman 40 plates and hydroquinone developer were used in all cases.

The photometer was the standard Moll instrument.*

The experimental method used in this work was as follows. The spectrum of the line group under investigation was photographed with an exposure time such that the densities of the components were in the region of normal exposure. The plate was then exposed for an *equal* time to the spectrum of a Nernst filament taken through a so-called neutral wedge placed directly before the slit of the spectrograph.

Uniform illumination of the slit for the wedge photograph is essential. This was assured by setting the Nernst filament in such a position that an exposure without the wedge in place resulted in uniform blackening across the image at any wave-length.

Moll photometer curves were obtained by running across the Stark components at maximum field, and at right angles across the wedge photograph in the same wave-length region, without changing the adjustment of the photometer.

Points could then be picked out on the wedge photometer curve which represented densities equal to the maximum densities of the components under investigation. The separation of any two points on the wedge curve corresponded to a definite length on the wedge, which was found from the magnification of the photometer and the focal lengths of the spectrograph lenses. The relative intensities (I_1/I_2) corresponding to these points was given by

$$\log I_1/I_2 = D_\lambda (l_2 - l_1),$$

where ($l_2 - l_1$) is the length on the wedge referred to above, and D_λ is the wedge density for the given wave-length and is found by calibration. The wedge used was of greenish-blue glass. The method of calibration has been described elsewhere.† The wedge density D_λ was :—

λ (Å)	4026	4388	4472	4922
D_λ (-/mm.)	0.535	0.426	0.376	0.301

* Moll, 'Proc. Phys. Soc.,' vol. 33, p. 207 (1921).

† Foster and Chalk, 'Proc. Roy. Soc.,' A, vol. 123, p. 108 (1929).

Variation of plate sensitivity with wave-length was assumed negligible over the small regions in question.*

There is some confusion in the literature† regarding the necessity of making the exposure times for the phenomenon and the intensity marks of equal length. Wedge photographs of the spectrum of a Nernst filament in which only the exposure time was varied showed that with the type of plate and procedure used by the author, equal exposure times were necessary.

‡The heights of the curves as they appeared on the photometer graph could not be taken as a true measure of the density. Several corrections had to be made.

(a) Lines which were so close together that their densities were mutually affected showed in the photometer graph as overlapping curves. True photometer curves were constructed for these by reflecting the uninfluenced side of the larger curve to the opposite side of its axis of symmetry, and subtracting the resulting values from the actual photometer curve. The method has been fully described by Ornstein, Kapuscinski and Eymers.‡

(b) Stark has objected§ to the fact that points of maximum blackening have been taken as a measure of the intensity. In this type of work the variation of field, which is always present, causes the outer components to become diffuse, and maximum blackening measurements give values for their intensities which are too low. Some correction is then necessary in the comparison of components of different displacements.

Let us consider the photometer curve for a photographic line produced by light of intensity i acting for a time t . The straight line character of the wedge photometer curves indicates that the relation $h = \alpha \log(i t)$ holds approximately where h is the height of the photometer curve and α is a constant. The area under a curve having the same abscissæ, but having ordinates $(i t)$ instead of $\alpha \log(i t)$ will be a measure of the energy associated with the line.

If we assume the average width ω (i.e., the area under the curve divided by its maximum height) to be the same for the photometer curve and for the energy curve, a correction can be made in the comparison of two lines of slightly different average widths.

* Jones and Sandvik, 'J. Opt. Soc. Am.,' vol. 12, p. 401 (1926).

† Ornstein, 'Proc. Phys. Soc.,' vol. 37, p. 334 (1925) and 'Phys. Z.,' vol. 28, p. 688 (1927); Dorgelo, 'Phys. Z.,' vol. 26, p. 756 (1925); Harrison, 'J. Opt. Soc. Am.,' vol. 19, p. 267 (1929); Dewey, 'Phys. Rev.,' vol. 30, p. 770 (1927).

‡ 'Proc. Roy. Soc.,' A, vol. 119, p. 781 (1928).

§ 'Ann. Physik,' vol. 5, p. 1009 (1929).

The maximum height of an energy curve of equal area but of some standard average width W is given by

$$IT = \omega it/W.$$

The height of the photometer curve corresponding to this is

$$\bar{h} = \alpha \log \omega/W + \alpha \log it = \alpha \log \omega/W + h.$$

Hence the correction Δh to be applied to a line of average width ω in order to compare it with one of average width W is given to the first order of small quantities by

$$\Delta h = (\omega - W) \alpha/W.$$

The average widths of the lines to be compared were obtained by determining the area under the photometer curves with a planimeter and dividing it by the maximum height of the curve.

The constant α depends upon a number of undetermined factors, but is easily obtained from each photometer graph of the wedge photograph by means of the relation

$$\alpha = \frac{(h_1 - h_2)}{(x_2 - x_1)} \cdot \frac{m}{D_{\lambda}},$$

where $(h_1 - h_2)$ is the measured difference in height between any two points on the curve separated by the distance $(x_2 - x_1)$, D_{λ} is the wedge density and m the magnification of the photometer.

This correction will always tend to be small for the more diffuse components since the densities of the edges of the photographic image will fall on the under exposed region of the characteristic blackening curve.

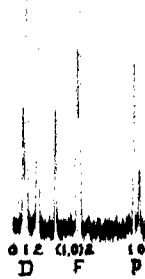
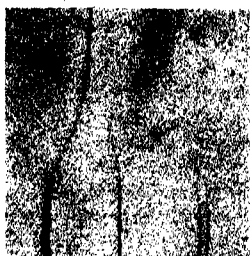
Correction (b) was found to make an appreciable difference only in the relative intensities of the F and f components of 2P — 5Q and 2p — 5q, and in the P components of 2P — 5Q.

A further source of error lies in the fact that the densities of the photographic plate are reliable to only about 3 per cent. owing to local variations in plate sensitivity, and to variations introduced in the developing process.*

If any error be introduced by the assumption that the plate sensitivity is constant over the small regions involved, it will tend to make the components toward one end of the spectrum appear too large and those toward the other end appear too small. No variation of this kind was observed.

Individual determinations should be good to 12 per cent. Values for very weak components, however, are apt to be relatively inaccurate, since their

* Schell, 'Ann. Physik,' vol. 35, p. 695 (1911); Harrison, 'J. Opt. Soc. Am.,' vol. 19, p. 267 (1929).

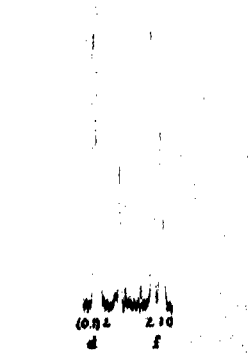
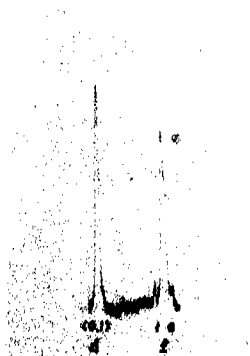
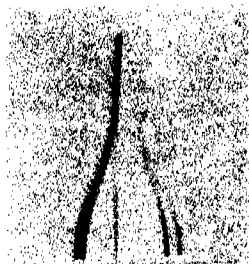
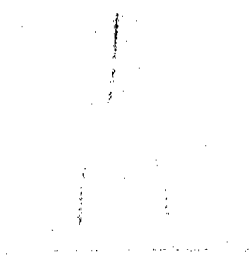


Group 2P-4Q.

Parallel Components.

Perpendicular Components.

Field strength 52.0 kv./cm.

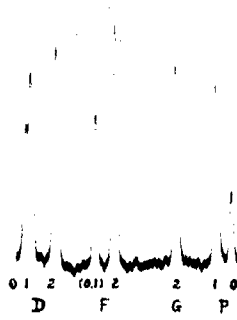
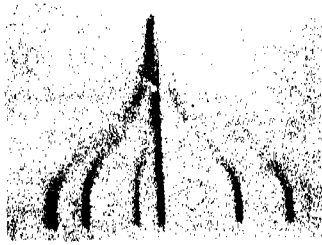


Group 2p-4q.

Parallel Components.
Field Strength 56 kv./cm.

Perpendicular Components.
Field Strength 59.1 kv./cm.

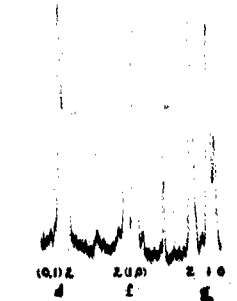
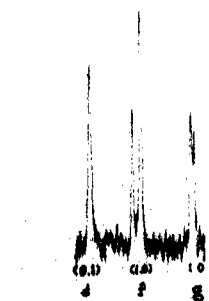
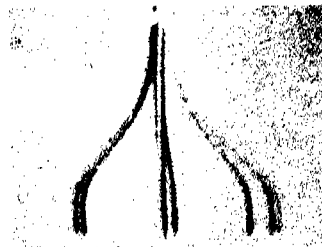
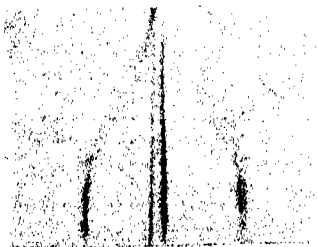
(Facing p. 80.)



Parallel Components.
Field strength 52.8 kv./cm.

Group 2P-5Q.

Perpendicular Components.
Field strength 55.0 kv./cm.



Parallel Components.
Field strength 30.5 kv./cm.

Group 2p-5q.

Perpendicular Components.
Field strength 46.3 kv./cm.

densities as well as those of the corresponding intensity marks lie in the region in which the blackening law first shows a departure from the logarithmic form.

The field strengths which were obtained by measuring the displacements and comparing with the theory* are in error by less than 3 per cent. In the region of 50 kilovolts per centimetre this will not in general affect the theoretical values given in Table II, and at the most will change only the last figure.

Results.

A comparison between theory and experiment is given in numerical form in Table II and in graphical form in fig. 3. The ratios were adjusted by making

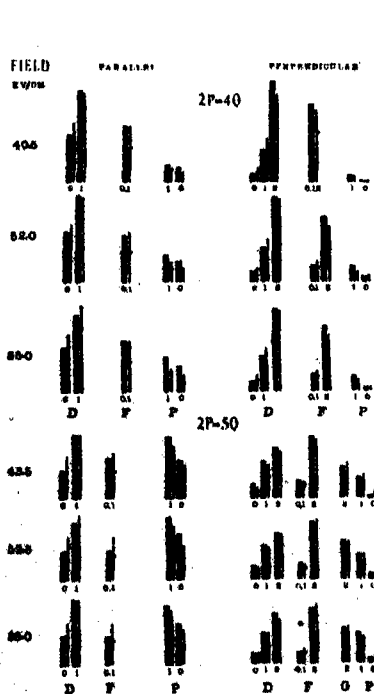


FIG. 3.—Comparison of theoretical and experimental intensities of Stark components of two parahelium line groups. The heavy lines denote experimental values. When two components are unresolved the sum of their theoretical intensities is plotted and the intensity of the stronger is indicated by a horizontal bar.

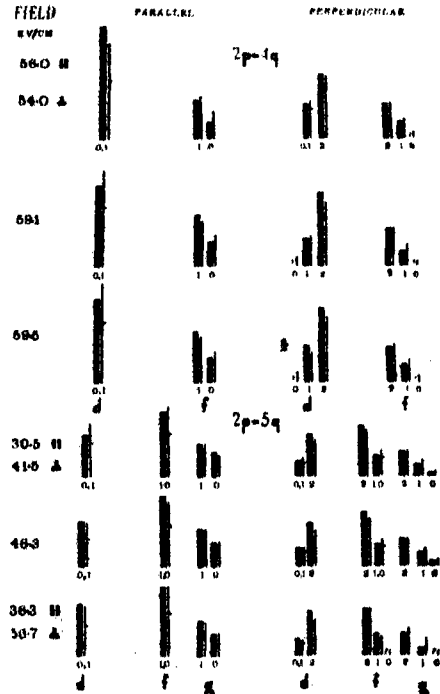


FIG. 4.—Comparison of theoretical and experimental intensities of Stark components for two orthohelium line groups.

* Foster has shown that theory and experiment are in good agreement in this respect.

Table II.
2P — 4Q (λ 4922).

Field in kv./cm.	Change in m.	Parallel components.						Perpendicular components.					
		D.		F.		P.		D.		F.		P.	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
40.5	2-1	—	—	—	—	—	—	0.380	0.44	0.220	0.34	—	—
	1-1, 1-0	0.390	0.40	0.150	0.078	0.060	0.078	0.190	0.14	0.073	0.28	0.030	0.031
	0-0, 0-1	0.260	0.21	0.096	0.066	0.045	0.066	0.065	0.038	0.023	—	0.012	0.005
52.0	2-1	—	—	—	—	—	—	0.360	0.37	0.240	0.28	—	—
	1-1, 1-0	0.375	0.38	0.135	0.12	0.087	0.12	0.185	0.15	0.068	0.073	0.044	0.067
	0-0, 0-1	0.250	0.22	0.080	0.089	0.064	0.089	0.064	0.045	0.020	—	0.019	0.016
55.0	2-1	—	—	—	—	—	—	0.360	0.37	0.240	0.28	—	—
	1-1, 1-0	0.375	0.33	0.130	0.16	0.095	0.16	0.185	0.15	0.066	0.076	0.048	0.069
	0-0, 0-1	0.250	0.19	0.078	0.11	0.069	0.11	0.064	0.043	0.020	—	0.020	0.021

Table II—(continued).
 $2p - 4g$ (λ 4471).

Field in kv./cm.	Change in m.	Parallel components.			Perpendicular components.		
		d .		f .	d .		f .
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
p 56.0 • 54.0	2-1 1-1, 1-0 0-0, 0-1	— 0.340 0.220	— 0.66 }	— 0.250 0.170	— 0.23 0.097	0.370 0.175 0.055	0.215 0.125 0.042
	2-1 1-1, 1-0 0-0, 0-1	— 0.335 0.220	— 0.46 }	— 0.255 0.175	— 0.29 0.14	0.360 0.170 0.055	0.220 0.130 0.043
	2-1 1-1, 1-0 0-0, 0-1	— 0.335 0.220	— 0.47 }	— 0.255 0.175	— 0.29 0.14	0.360 0.170 0.055	0.220 0.130 0.043
59.1 59.5	2-1 1-1, 1-0 0-0, 0-1	— 0.340 0.220	— 0.66 }	— 0.250 0.170	— 0.23 0.097	0.370 0.175 0.055	0.215 0.125 0.042
	2-1 1-1, 1-0 0-0, 0-1	— 0.335 0.220	— 0.46 }	— 0.255 0.175	— 0.29 0.14	0.360 0.170 0.055	0.220 0.130 0.043
	2-1 1-1, 1-0 0-0, 0-1	— 0.335 0.220	— 0.47 }	— 0.255 0.175	— 0.29 0.14	0.360 0.170 0.055	0.220 0.130 0.043

Table II—(continued).

$2p - 5q$ (λ 4026).

Field in kv./cm.	Change in m.	Parallel components.						Perpendicular components.					
		d.		f.		g.		d.		f.		g.	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
p 30.5 s 41.5	2-1 1-1, 1-0 0-0, 0-1	— 0.185 0.115	— 0.23 —	— 0.235 0.150	— 0.36 —	— 0.180 0.120	— 0.18 0.14	0.200 0.080 0.024	0.23 — —	0.255 0.110 0.035	0.28 — —	0.145 0.100 0.035	0.14 0.074 0.022
	2-1 1-1, 1-0 0-0, 0-1	— 0.145 0.080	— 0.24 —	— 0.215 0.135	— 0.38 —	— 0.200 0.135	— 0.20 0.13	0.195 0.075 0.022	0.23 — —	0.255 0.110 0.033	0.29 — —	0.150 0.100 0.035	0.15 0.076 0.029
	2-1 1-1, 1-0 0-0, 0-1	— 0.165 0.105	— 0.28 —	— 0.230 0.145	— 0.37 —	— 0.185 0.125	— 0.19 0.12	0.195 0.065 0.019	0.24 — —	0.255 0.104 0.032	0.25 0.12 —	0.150 0.105 0.036	0.12 0.04(?) ?

the sum of the experimental intensities equal to that of the theoretical intensities for the observed components. The experimental value for two components which are not visibly resolved on the plate should lie between the intensity of the strongest and the sum of the intensities of the components.

Consistent differences of the experimental values from those predicted by theory are probably significant, even when they fall within the limit of experimental error.

Intensity relations in the Stark effect have been reported* to vary with the direction of the applied electric field relative to the direction of motion of the particles in the discharge tube, and with the direction of observation. No attempt has been made by the writer to study these effects. In all cases the direction of observation was perpendicular to the field.

Group 2P — 4Q (λ 4922).

In this group there are several consistent variations from the predicted values. The most noticeable is the tendency of the $P_{1 \rightarrow 1}$, $P_{0 \rightarrow 0}$ and $P_{1 \rightarrow 0}$ components to appear too strong experimentally by from 30 to 60 per cent. The $D_{0 \rightarrow 0}$, $D_{1 \rightarrow 0}$ and $D_{0 \rightarrow 1}$ components are all too weak by 20 or 30 per cent. Dewey found the sum of the intensities of the unresolved P components to be too strong by about 60 per cent., and the sum of the F components in the perpendicular polarisation to be from 15 to 30 per cent. too strong.

In Plate 7, a typical photograph of this group shows all components except $F_{1 \rightarrow 1}$, $F_{0 \rightarrow 0}$ and $F_{1 \rightarrow 0}$, $F_{0 \rightarrow 1}$, clearly resolved.

Group 2P — 5Q (λ 4388).

Here the variations from theory are not so great as in 2P — 4Q. The $P_{1 \rightarrow 1}$ and $P_{0 \rightarrow 0}$ components are still consistently strong, but only by about 15 per cent. The $D_{0 \rightarrow 0}$ component appears to be about 25 per cent. too weak.

Plate 8 shows all components resolved excepting the $F_{1 \rightarrow 1}$, $F_{0 \rightarrow 0}$ and the $F_{1 \rightarrow 0}$, $F_{0 \rightarrow 1}$ components. It is interesting to notice in this plate the presence of one of the vanishing components. This is seen in the case of the G components in the parallel polarisation. The theory predicts that they vanish when their displacement is equal to that of the P — P line at zero field. The photograph shows that this is confirmed by experiment. The reappearance of the components at higher fields has been observed by Foster.

* Wierl and Mark, 'Z. Physik,' vol. 53, p. 526 (1929) and vol. 57, p. 494 (1929); Stark, 'Ann. Physik,' vol. 5, p. 607 (1930) and vol. 5, p. 665 (1930).

Group 2p — 4q (λ 4471).

This group was the most difficult to resolve, and the results are less satisfactory than for the others. The values for the $f_{0 \rightarrow 0}$ and $f_{1 \rightarrow 0}$ components appear to be too low by about 20 per cent. Dewey found the intensity for the unresolved f components to be too low by 20 or 30 per cent. in both polarisations.

Plate 7 shows a partial resolution of $d_{1 \rightarrow 1}$, $d_{0 \rightarrow 0}$ and $d_{1 \rightarrow 0}$, $d_{0 \rightarrow 1}$. The other components are resolved.

Group 2p — 5q (λ 4026).

Here the $g_{1 \rightarrow 0}$ and the $g_{0 \rightarrow 1}$ components were experimentally too weak by about 25 per cent., while the $d_{2 \rightarrow 1}$ component was about 15 per cent. too strong. Dewey found the unresolved g components to be 20 to 40 per cent. too weak, and the unresolved f components to be from 15 to 60 per cent. too strong.

In Plate 8 all components except $d_{1 \rightarrow 1}$, $d_{0 \rightarrow 0}$; $d_{1 \rightarrow 0}$, $d_{0 \rightarrow 1}$; $f_{1 \rightarrow 1}$, $f_{0 \rightarrow 0}$; and $f_{1 \rightarrow 0}$, $f_{0 \rightarrow 1}$ are clearly resolved. The weak lines appearing at either side of the $f_{1 \rightarrow 0}$ components are fine structure lines.

It should be mentioned that Dewey found the unresolved $p - p$ combination lines to be experimentally too strong by from 200 to 300 per cent. in both orthohelium line groups. These components were not investigated by the writer.

Enlargements of typical plates with their corresponding photometer graphs are shown in Plates 7 and 8. The lateral magnification of the photometer was reduced to eight for the published graphs, but in all experimental work a magnification of 50 was used. Due to corrections for overlapping photometer curves and diffuse components the true heights of some of the photometer curves will differ from those shown in Plates 7 and 8, but the correction in height is small.

Discussion.

For field strengths ranging from 30 to 60 kilovolts per centimetre the theory predicts intensities for the individual components which are for the most part in agreement with the experimental values. The discrepancies which do appear are given in Table III.

The observed discrepancies fall into two general classes: first, those which appear to the same degree in all the components of a line, and secondly, those which appear only in certain components of a line, while the other components agree with the predicted values. The first class may be considered as arising

Table III.

Group.	Component.	Approximate variation.
2P — 4Q	All P's	50 per cent. strong
	D ₀ →0, D ₀ →1, D ₁ →0	20 per cent. weak
2P — 5Q	P ₁ →1, P ₀ →0	15 per cent. strong
	D ₀ →0	25 per cent. weak
2p — 4q	Unresolved p's	200 per cent. strong (Dewey)
	f ₀ →0, f ₁ →0	20 per cent. weak
2p — 5q	Unresolved p's	200 per cent. strong (Dewey)
	d ₂ →1	15 per cent. strong
	g ₁ →0, g ₀ →1	25 per cent. weak

from phenomena closely associated with the azimuthal quantum number, and the second class as arising from phenomena associated with the magnetic quantum number.

It is extremely unlikely that the method of calculating the probabilities of transition ("theoretical intensities") is at fault. It seems far more probable that the observed variations are due to the failure of some basic assumption.

A fundamental point in the theory is the assumption that the number of atoms excited to the different states of the same total quantum number is the same. It appears that this is not true, and that certain favoured states exist. On this basis the discrepancies of the first class (*i.e.*, P — P and p — p lines) receive the following satisfactory qualitative explanation.

The problem of intensities in the normal helium spectrum has been studied by many investigators* and it has been well established that the relative intensities of the permitted lines vary with the conditions of excitation. At high pressures atomic impact and culminative excitation play important rôles; but at low pressures, where the mean free path is long and the energy of the impinging electron great, direct excitation is the chief factor. It is difficult to predict just what part each type played in the present experiments, but it is reasonable to assume that direct excitation was an important factor.

Ornstein and co-workers have shown that a selection rule ($\Delta k = \pm 1$), less

* Hughes and Low, 'Proc. Roy. Soc.,' A, vol. 104, p. 480 (1923); Bazzoni and Lay, 'Phys. Rev.,' vol. 23, p. 327 (1924); Udden and Jacobsen, *ibid.*, vol. 23, p. 322 (1924); Hodges and Michels, *ibid.*, vol. 32, p. 913 (1928); Ornstein, Burger and Kapuscinski, 'Z. Physik,' vol. 51, p. 34 (1928); Peteri and Elenbaas, *ibid.*, vol. 54, p. 92 (1929); Hanle, *ibid.*, vol. 56, p. 94 (1929); Burger, *ibid.*, vol. 54, p. 643 (1929).

rigid than that for radiation, is followed in transitions due to electron impact. Additional support for this theory has been found by Peteri and Elenbaas.

The selection rule for radiation breaks down in an electric field and new helium lines appear with intensities which can be calculated. It seems not unlikely that the selection rule for impact transitions is affected *to no greater extent*.

This appears from a consideration of the following facts. The probability of radiation transitions is a function of the atomic levels and the field strength. It is reasonable to assume that in impact transitions the characteristics of the impinging electron must also be considered.* Since the levels of a group lie close together, however, the relative probabilities of impact transition should be affected very little by the velocity distribution of the exciting electrons.

In the normal spectrum radiation transitions to the ground level 1S (or 2s) are restricted to the initial levels *nP* (or *np*). In electric fields of the order of 40 kilovolts per centimetre this restriction is removed, although transitions from the *P* (or *p*) states are still enormously favoured.

The approximate probabilities of direct excitation to the different levels of a group as calculated by matrix mechanics are given in Table IV.

Table IV.—Probability of Direct Impact Transition in a Field of 40 kv. per centimetre.

Parhelium.

Transition.	S.	D.	F.	G.	P.
4Q — 1S	0.0018	0.053	0.065	—	0.88
5Q — 1S	0.017	0.093	0.15	0.26	0.48

Orthohelium.

Transition.	s.	p.	d.	f.	g.
4q — 2s	0.0004	0.99	0.0040	0.0018	—
5q — 2s	0.0066	0.93	0.027	0.020	0.011

The intensity of the groups 2P — 4Q, 2P — 5Q, and 2P — 6Q is observed to fall off rapidly with the increasing principal quantum number of the initial

* Fues, 'Phys. Z.', vol. 29, p. 852 (1928), has discussed the problem from the standpoint of the intensity ratios in multiplets, in which the spins of the exciting and orbital electrons enter.

state. This suggests that the P levels will be less strongly excited, and the *p* levels more strongly excited than given in Table IV since their separation from the other levels of the group is relatively large.

The process of indirect excitation is extremely complicated. However, since it begins with a transition from a P (or *p*) state, we might expect an excess of atoms to be excited to the S, P and D (or *s*, *p* and *d*) states. The F and G (or *f* and *g*) states will be less favoured in the order named.

If we assume that direct excitation plays an important part the following variations from theory may be expected :—

1. The only lines which will show very large variations from the theory are the P and *p* lines.
2. The *p* lines of orthohelium will show much larger variation than the P lines of parhelium.
3. The variation of the P lines in $2P - 4Q$ will be *considerably greater* than that of the P lines in $2P - 5Q$, but the variation of the *p* lines in $2p - 4q$ and $2p - 5q$ will be *approximately the same*.

Reference to Table III shows that these details are found experimentally.

It is not clear how the *m* value may enter in excitation, so that discrepancies of the second class are unexplained. Table IV shows, however, that certain other lines should show relatively small variations from the theory. These variations are in all cases in the direction which is indicated by the observed variation in a component, but no reason is apparent why certain components only should vary.

Summary.

1. A new modification of the Lo Surdo source which has a uniform field throughout an appreciable portion of the Crookes' dark space has been developed.

2. The experimental relative intensities of the Stark components of four selected helium line groups have been determined by a photographic-photometric method.

3. A method has been suggested for correcting for the diffuse character of the outer components due to field variations.

4. The theoretical relative intensities of the components of the selected groups are given at six field strengths between 10 and 100 kilovolts per centimetre.

5. A comparison of theory and experiment indicates good agreement for most components. There are, however, definite discrepancies. These are

of two general types: (a) that in which the variation from theory occurs to the same extent in all the components of a line, and (b) that in which only a certain component (or components) of a line shows a variation.

6. The first of these receives a satisfactory qualitative explanation on the assumption that the selection rule for impact transition breaks down in the presence of an electric field to no greater extent than is indicated by the Stark effect in emission. No explanation has been found for the second type of discrepancy.

In conclusion the writer wishes to thank Dr. J. S. Foster for the suggestion of the problem and for encouragement and advice throughout the entire course of the work. His thanks are also due to Dr. L. Chalk for the use of wedge calibration plates, and to the National Research Council of Canada whose awards enabled this work to be carried out.

*The Optical Determination of High Metallurgical Temperatures—
The Melting Point of Iron.*

By C. H. M. JENKINS, D.Sc., and MARIE L. V. GAYLER, D.Sc.

(Communicated by W. Rosenhain, F.R.S.—Received May 15, 1930.)

The present investigation has been carried out in the Metallurgical Department of the National Physical Laboratory in order to adapt the optical pyrometer to the estimation of the fusion temperatures of materials of high purity and high melting point and of substances of corrosive or volatile nature. Melting points and thermal changes in the solid state at high temperatures are generally determined by means of platinum thermocouples which are protected from the molten metal or its vapour by insertion in a refractory sheath. Contamination of the molten metal is frequently occasioned by chemical attack which takes place between the metal and the refractory crucible or couple sheath. This is particularly marked when the refractories contain siliceous material.

The determinations of the melting points of series of binary alloys of iron which are being carried out for the Ferrous Alloys Research Committee in the Metallurgical Department necessitated the accurate determination of the

melting point of iron, since that metal forms the basis of the research. Iron was, therefore, chosen as the most suitable metal with a high melting point on which to base the development of the optical pyrometer method.

Throughout this research contact has been maintained with the Heat Department of the National Physical Laboratory. In particular the authors desire to thank Mr. F. H. Schofield for his advice and assistance on theoretical considerations.

I. Experimental Considerations.

Difficulties arose during the examination of the two binary metallic series of alloys, iron-manganese and nickel-chromium, caused by the ready volatility and corrosive action of manganese and from the rapid attack of chromium on the majority of refractories. The successful use of the thermocouple method involved the production of gas-tight thermocouple sheaths which would not only exclude metallic vapour but would also be impervious to hydrogen, the gas which was used for maintaining the alloys in a reducing atmosphere. The preparation of these sheaths proved to be a difficult matter because it was not only necessary to make them gas-tight in order to prevent the reduction of any siliceous material which might cause contamination of the platinum, but it was also necessary that they should be made of material free from silica, since there was a danger of contamination of the melt also from silica. No thermocouple sheaths were produced which were both impervious to metallic vapour and hydrogen, and at the same time unattacked by the molten metal. The most hopeful material, however, consisted of a mixture of 35 per cent. of lime with 65 per cent. of alumina. Although pure iron or pure manganese did not attack this material, reasonably long lengths of tubing or rod could not be produced. Some material which was reasonably gas-tight was, however, produced by firing very short lengths of the extruded tube at a temperature of 1710° C. In view of difficulties of this kind which beset the use of thermocouples in such circumstances, the authors were led to adopt the optical pyrometer.

The measurement of high temperatures by means of the disappearing filament type of optical pyrometer is accepted as an accurate means of determining temperature when the instrument can be sighted upon a surface within a "black-body" enclosure.* The present paper deals with the adaptation of this method to the experimental conditions met with in metallurgical investigations.

* Fairchild, Hoover and Peters, 'Bur. Standards J. Research,' vol. 2, p. 931 (1929); Schofield, 'Proc. Roy. Soc.,' A, vol. 125, p. 517 (1929).

The optical pyrometer in its various forms is used extensively in works and laboratories for the measurement of the temperatures of radiating surfaces. Under such conditions the degree of accuracy required is not great, and the optical method is probably less accurate than a platinum-platinum rhodium thermocouple. The inaccuracy is due to the presence of flame, or hotter or colder objects, near the surface of the material under observation.

In the determination of a melting point by an optical pyrometer, a number of different arrangements have been employed.* The two most common of these may be described as follows:—

1. *The "Wire" Method.*—The hot junction of a strip of the desired metal is inserted in a thermocouple which is placed in a black body enclosure situated in a suitable furnace. During the heating a continuous record is taken of the E.M.F. of the couple and of the temperature of the black body enclosure as shown by the optical pyrometer. The melting point of the metal is indicated by the failure of the E.M.F. of the thermocouple to follow the increase of temperature. With a slight further increase of the temperature of the black body the metallic circuit is broken by the severance of the metallic strip.

2. *The "Ingot" Method.*—A closed tube is immersed in the centre of a mass of metal. In this tube suitable baffles or constrictions are formed which permit the sighting of the pyrometer through a series of observation holes. The temperature of melting is indicated by the absorption of heat on raising the temperature of the furnace in the same manner as in the thermocouple method.

In the present research the ingot method has been chiefly used although a certain number of determinations have been made by the wire method. A modification of the ingot method, suggested by Dr. W. Rosenhain,† has also been tried. In this arrangement the black body enclosure is formed by the inside of a gas bubble blown on the end of a tube immersed in the liquid.

The capacity of the crucibles used ranged from 8 mls. for the smallest to 24 mls. in the case of the largest pot. Agreement has been obtained between the results from the various methods.

The Optical Pyrometer.—The pyrometer used was of the disappearing filament type designed by Holborn and Kurlbaum. This was fitted with a red glass screen, which diminished the intensity of illumination from both the black body enclosure and the filament of the lamp.

The general arrangement of the apparatus is shown diagrammatically in

* Hoffmann and Meissner, 'Ann. Physik,' vol. 60, p. 20 (1919); Fairchild, Hoover and Peters, *loc. cit.*; Schofield, *loc. cit.*

† W. Rosenhain, 'J. Inst. Metals,' vol. 2, p. 36 (1929).

fig. 1. In this figure the light from the source either A_1 or A_2 is reflected by the prism B into the lens C which is the objective of the pyrometer. The lens

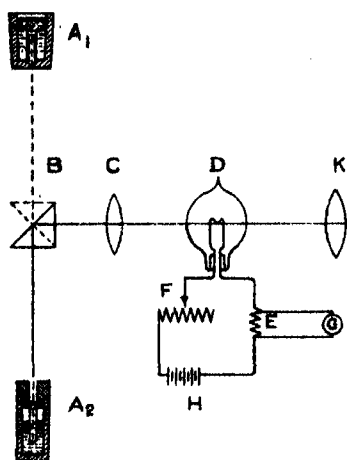


FIG. 1.—Either A_1 or A_2 used as source.

C brings the image of the source A_1 or A_2 into focus at the centre of the filament. The eyepiece magnifies both filament and source by approximately 5 diameters to facilitate colour matching. The temperature of the filament is adjusted by movement of the sliding resistance F; the resulting current flowing through the lamp is measured by a standard resistance block E and a potentiometer.

The red screen in the pyrometer has been made of the same glass as that used in the recent determination of the melting point of palladium by F. H. Schofield. It transmits light of a mean effective

wave-length of 0.656μ . This screen is referred to later in Section III in relation to the Sector Method.

When using the pyrometer at temperatures above 1550°C . a neutral absorption screen manufactured by Messrs. Leeds and Northrup has been inserted in the pyrometer to cut down the brightness of the source. Thus the lamp is capable of measuring high temperatures without being excessively heated, a condition which would bring about ageing.

IIA. *Methods Using Immersed Refractory Tubes.*

Preliminary investigations using small pieces of refractory tubing containing a certain amount of siliceous material indicated the necessity for the development of pure refractories. The size of this tubing was 2 mm. internal and 5 mm. external diameter. When immersed in the molten metal the tubing was usually found to react with the melt causing contamination; this reaction can be obviated by the use of pure oxides such as magnesia and alumina, etc. Also during the experiments a slight shift of the immersed tube occurred which caused the position of the filament relative to the sighting area to alter so that inaccurate observations were made. The displacement may be due to two causes: (1) shrinkage of the refractories which takes place apparently on account of the action of metallic vapour, even though the refractories had been previously fired at temperatures above those reached in the experiments.

(This is referred to later.) (2) After immersion in the molten metal the tube tends to lift on account of its buoyancy. This causes the axis of the tube to deviate from the vertical and results in difficulty in alignment of the pyrometer in subsequent observations. At the same time serious bending stresses are set up which shift the relative position of the "matching" area still further.

These factors indicate that the refractories must not only be of high purity which has the disadvantage that they are apt to be very friable but they must also be as hard as possible so that pots and tubes made of this shall be strong and will not distort in use. The importance of hard refractories for this work cannot be over emphasised.

The difficulty of shrinkage described above was overcome by the use of pure oxides suitably ground and fired at high temperatures; while the difficulty of maintaining the tubes in place was overcome in two ways: first, by using a moulded "head" or block formed of a rigid mass of refractory in which the tube is held and second by using tubes moulded as part of the pot, projecting upwards from the base, thus avoiding any discontinuity in the base of the crucible. This arrangement gives the tube more rigid support. Pure oxides such as alumina, thoria, magnesia, etc., are not readily formed into crucibles even of the simplest shape. The design of black body enclosures is thus largely influenced by the necessity of providing for the removal of the very tender freshly pressed pot from the mould in which it has been formed.

In the present design of refractories the diameter of the immersed tube was large in comparison with the diameter of the orifice in the baffle-plugs, which was in no case greater than one-eighth of the depth of immersion. The effect of the depth of immersion of the refractory tube is rather different in the case of the optical method as compared with the thermocouple method. In the latter case the temperature of the metal adjacent to the top of the thermocouple wires is really being measured and it is only necessary to prevent conduction along the wires apart from the surface loss by radiation. In the case of the optical method, however, the observed temperature is the average temperature of a relatively large enclosure; and that when black body conditions have been attained by a sufficient depth of immersion, further immersion does not improve the conditions of measurement. The insertion of a baffle plug facilitates the attainment of black body conditions without employing large depths of immersion.

For example the reduction of the apparent temperature by departure from black body conditions in the absence of a baffle plug is illustrated in the case of the experiment upon iron. The mean temperatures of melting and freezing

were found to be as low as 1507°C . and 1504°C . respectively, when observations were made sighting either into the black body head as shown in fig. 2 or from above into the top of the tube held in the centre of the large crucible as shown in fig. 3. When baffle-plugs were inserted, the observed mean temperatures were raised to 1527°C .

Considerable attention has been devoted over a period of some years to the development in the Metallurgical Department of pure refractories in connection with the metallurgical researches in progress. This work has been in the charge of Mr. D. Turner to whom the authors are indebted for the preparation of the ground material and the firing of the refractories as well as for co-operation in the production of the pots.

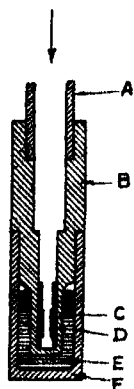


FIG. 2.

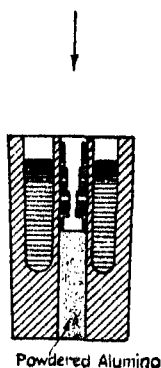


FIG. 3.



FIG. 4.

After preparation of the baffle, a flat is ground longitudinally on the surface to allow circulation of gas.

The pure alumina used for the preparation of the refractories in the present research was obtained from the British Aluminium Company. The analysis of this material showed that the only impurity present was a trace of iron, *i.e.*, less than 0.01 per cent. The material which in the condition as received passes through a 120-mesh sieve was ground to a very fine powder in an end runner mill after which it was magnetically separated to remove any traces of iron which might have been introduced by grinding. The powder which would entirely pass a 200-mesh sieve was then made damp with water and pressed into the mould by gradual filling and repeated intermediate ramming. The chief difficulty lies in the successful extraction of the pot from the mould. It is essential that all the portions of the refractory object are sustained in slight compression during the extraction process.

The mould for making the pot shown in fig. 2 opens in three pieces to allow the head to be removed. The central tube in the refractory head is formed by a metal pin which is withdrawn before the mould is opened.

In the case of pots in which the central tube is rigidly fixed, the shape of the internal ring is formed by a polished brass core around which the material is packed. The arrangement of the mould and core is shown in fig. 5. Great care is needed in extracting this core; for this purpose the whole mould is held in a screw press which exerts a downward push on the top of the central tube while the core is being pulled out. The pot is then removed from the main cylinder by pushing the base plate upwards. The centre pin 3 is then pulled out before lifting the pot from the base. The crucibles are then fired at a temperature of 1530°–1560° C.

The types of crucibles, tubes and heads and their respective "baffles" are shown in section in figs. 2 to 4 inclusive.

In the form shown in fig. 2 the immersed tube C constitutes a part of the block of refractory material B which rests in the crucible. The mass of this block is sufficient to keep the tube in position. The molten metal E is contained in a hard refractory crucible F whose normal capacity is about 8 ml. The tube C which is held centrally in the pot contains a perforated refractory plug D which acts as a "baffle" and prevents excessive loss of heat by radiation. This baffle-plug has a small axial aperture which is reduced in diameter by steps so as to facilitate the sighting of the pyrometer as illustrated in fig. 2.

Considerable difficulty was at first experienced in the original form on account of the fracturing of the tip C at the sharp junction which it had then formed with the main block B. This was remedied later by the provision of a suitable curvature at this point.

In the arrangement described above and also in that shown in fig. 3 the optical pyrometer is sighted from above. In the arrangement shown in fig. 3 the black-body chamber is formed by the insertion of the baffle-plug in the tube which forms a part of the crucible. The tube passes through the entire depth of the pot, but before use the lower half is tightly packed with powdered alumina from the bottom to within 1½ inches from the top of the crucible. The capacity of this crucible is about 24 ml. in the normal working position.

In the form of apparatus shown in fig. 4 the pyrometer is sighted from

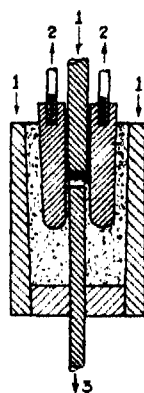


FIG. 5.

below the crucible. The tube whose closed end is totally immersed in the molten metal projects upwards about $\frac{3}{4}$ inch from the bottom of the crucible. The "baffle" used in this pot is the same as that shown in fig. 3 and it is held in position by placing the crucible on a refractory block containing a slightly smaller hole than that in the crucible. The same form of crucible tube and baffle was also used in a somewhat smaller size.

In this research two effects, due to the presence of metallic vapour have been observed (1) the shrinkage of refractories, (2) the absorption of light by metallic vapour resulting in the lowering of the observed melting points. These effects may have been only slight in previous investigations possibly owing to the fact that the refractory black body chambers used in the course of those determinations were of such a compact nature that the diffusion of metallic vapour through their walls was inhibited. In the present research, however, it was necessary to use refractory bodies of a special nature and these were somewhat porous; consequently metallic vapours could diffuse through them more readily.

This was clearly shown for instance when a black body head was examined after it had been immersed in gold and kept just below its melting point for several hours. The colour of both the tube of the head and the baffle-plugs inside was changed from white to a pinkish tinge, which suggested the possibility of the condensation of fine metallic particles from previously existing vapour. Furthermore, baffle-plugs made from refractories containing a certain amount of siliceous material were found to shrink during use in the presence of iron vapour while baffle-plugs made of pure hard alumina showed no visible shrinkage in similar circumstances. This also suggests that the metallic vapour is a possible cause of shrinkage.

The second effect observed, which was attributed to the presence of metallic vapour, was first noticed during the course of some observations on the melting point of gold. In this determination the small-sized black body head (see fig. 2) was used and six observations were made, three on cooling and three on heating through the melting point. The individual temperatures of the arrests which were taken on cooling and heating respectively agreed amongst each other to within less than 0.5° C., whereas the mean value of the results observed on cooling through the melting point was 1.5° C. lower than that on heating. The apparatus, in which this experiment was carried out, was then kept for a further 20 hours at a temperature just below the melting point of gold and then further observations were made. During six observations the melting point became successively lowered. The difference, for example,

between the temperature of the first and last values obtained by cooling through the melting point was 4° C. approximately, and by heating through the melting point $1\frac{1}{2}^{\circ}$ C.

In order to check the above results on gold, similar experiments were carried out using a pot, of the type shown in fig. 3. The gold was kept molten for a period of 2 days except for purposes of observation during freezing and melting. The temperature at which fusion occurred was observed at intervals of 24 hours and 48 hours after the initial melting and freezing. The results are plotted in fig. 10. The temperature of the melting of the gold was found to be depressed 1.8° C. when observations were taken 24 and 48 hours after the initial readings, and then a further 4° C., while the temperature of freezing was depressed 1.8° C. and a further 2° C.

The actual presence of vapour in the black-body chamber does not affect the apparent temperature, but if the vapour passes into the sighting tube above the black-body chamber which is at a slightly different temperature, then condensation of the vapour can occur. The fog, caused by this condensation will consist of small metallic particles which will be at a different temperature from that of the black-body and consequently the apparent temperature will not be that of the black-body. Hence in the above case the vapour from the gold must have formed a fog in the slightly cooler portion of the "sighting" tube.

On examination of the black-body head after these two sets of experiments it was noticed that instead of being white, the colour of the refractory had become a pale pink, and that this coloration penetrated through the material so that the baffles were also coloured. This confirmed the impression that gold particles were the cause of the apparent lowering of the melting point of gold, for the black-body conditions were otherwise excellent.

Under apparently satisfactory conditions discrepancies also occurred in the determination of the melting point of pure manganese, which is found to give off vapour very freely. In this case, however, the matching of the black-body area with the filament of the optical pyrometer presented difficulties not observed in the case of gold. It appeared as if the sighted area was being "fogged" and this was evidently due to the vapour which could be observed coming off from manganese and which was condensing in the colder part of the sighting tube as a dense fume.

A method for avoiding the effect of metallic vapour was then devised and in subsequent work was found to be satisfactory. If the black-body chamber, on which "sighting" occurs, is kept ventilated by a slow stream of gas then

any metallic vapour is removed which would otherwise tend to diffuse up the sighting tube.

If, however, a bubble of gas is blown and maintained in a molten metal, it will probably be more or less saturated with metallic vapour. In the case of iron neither in the bubble method nor in the black-body refractory method has appreciable effect of metallic vapour been observed; but it seems highly

probable that metallic vapour may be one of the factors of unsatisfactory results being obtained in the pot method in the case of gold and palladium.

According to the published data relating to the vapour pressure of metals at their melting points, this effect should be as marked in the case of iron as of gold since, at their respective fusion temperatures,* the vapour pressure of iron is higher than that of gold.

On account of the possibility of absorption of light by metallic vapour or fog which may enter the sighting tube, the pots have been erected in the furnace in such a manner that a stream of a suitable gas could be circulated through the apparatus sweeping any metallic vapour out of the line of sight.

In the case of the pot of the type shown in fig. 4 the crucible has been placed on refractories in the manner indicated in fig. 6. In this arrangement the light from the closed end of the tube is reflected into the horizontally held pyrometer by means of a right angle prism A which is fixed on a water-cooled metal plate by means of wax of high melting point. The

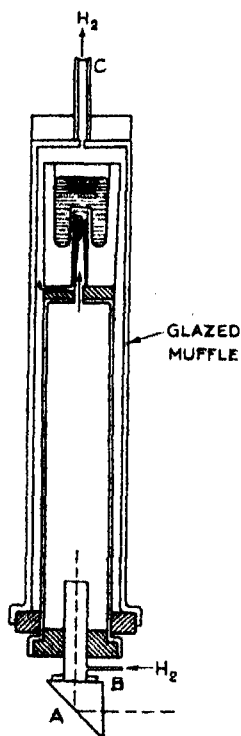


FIG. 6.

gas enters just above the prism from a tube marked B. A hole is drilled in the end of the smaller container so as to allow observation and also to permit the passage of gas through the baffle-plug. A flat surface has been ground on one side of the baffle-plug and a radial groove has been cut in the base of the pot to allow the gas to flow through the sight hole. The path of the gas through the baffle-plug is indicated by arrows in fig. 6. The gas stream passes into the space between the two containers and afterwards out by the tube C. This tube is also used to introduce "inoculating" material into the crucible so as to prevent undercooling of the liquid.

* "International Critical Tables," vol. 3, p. 205.

In the case of the refractory head illustrated in fig. 2 the gas was passed through the apparatus in the manner indicated in fig. 7. The gas is led down the sighting tube to the tops of the baffle-plugs which are shaped as shown previously in fig. 2. The convection current is sufficient to bring the metallic vapour into the stream of gas passing across the top of the refractory baffle-plug and thus the vapour is swept into the furnace.

The general method of procedure for taking observations was similar in all the experiments carried out in the course of the research. The metal used was heated or cooled through its fusion point at a rate of 2° to 3° C. per minute. Under these conditions the period of melting or freezing normally lasted 15 to 40 minutes. When using thermocouples for observing temperatures of fusion it is customary to observe the time taken for the temperature to rise or fall a definite amount. In the present method, however, observations of the temperature of the black body were taken at constant time intervals, *i.e.*, every minute. This ensured less eye-strain, for it is only necessary for the observer to "match" the filament of the pyrometer with the black body 10-15 seconds before the time signal so that during the remaining 45-50 seconds the eye may be resting. If the time taken for change of constant temperature is observed, the current through the filament of the lamp in the optical pyrometer is changed by a definite amount which corresponds to a definite change of temperature, and it is necessary to observe when the apparent temperature of the black body exactly matches this pre-determined temperature.

The eye-strain is far greater in this case since longer periods of observations are necessary in order that the eye may be sensitive to the exact matching of the filament and black body. Furthermore in the first method the current through the filament can be varied so that a comparison can be made from a higher or lower temperature; this facilitates matching to a marked degree.

From the observed temperatures taken every minute, time-temperature curves were plotted as shown in figs. 10 to 15, while the fusion temperatures are given in Table I.

The results obtained on gold, iron and palladium are given in Table I, columns 3, 7 and 8, while figs. 10 and 11 show typical time-temperature curves.

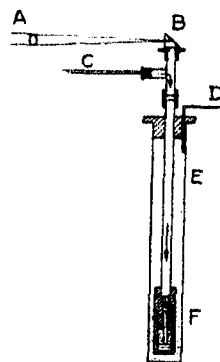


FIG. 7. — A. Optical Pyrometer. B. Prism. C. Entry for gas blown down on baffles. D. Entry for gas in which to melt the metal. E. Muffle. F. Black body head in melt.

Table I.

Average value of curve determinations.	Squatting wire method.	Sighting into tube formed in black body head (see fig. 2).		Molten surface or bubble method (see fig. 8).	Sighting into the top of a tube held in base of crucible (see fig. 3). Tube with baffles.	Sighting into tube formed in base of large crucible (see fig. 4).		Melting point derived.
		Tube with baffles.	Sector method.			Tube with baffles.	Sector Method.	
Gold. Melting point 1063° C.								
Heating.....	—	+1° C. : 3 : 57	—	1062 : 1 : 10	—	+2° C. : 6 : 123	—	Accepted value 1063° ± 1° C.
Cooling.....	—	-1° C. : 3 : 61	—	1053 : 1 : 17	—	-2° C. : 5 : 112	—	
Mean	1063 assumed	1063 : 6 : 118 assumed	—	1058 : 2 : 27	—	1063 : 11 : 235 assumed	—	
Iron.								
Heating.....	1493	1527 : 3 : 42	1529 : 4 : 55	1528 : 3 : 36	1528 : 2 : 22	1527 : 3 : 37	1524 : 2 : 22	1527° ± 3° C.
Cooling.....	—	1525 : 3 : recal.	1525 : 2 : 19	1537 : 6 : recal.	1526 : 2 : 24	1526 : 3 : 61	1530 : 2 : 21	
Mean	—	1526 : 6 : 46	1527 : 6 : 74	1528 : 9 : 42	1527 : 4 : 46	1526 : 6 : 98	1527 : 4 : 43	
Palladium. Melting point 1555° C.								
Heating.....	$\left. \begin{matrix} 1552 \\ 1558 \\ 1553 \end{matrix} \right\}$	—	—	—	—	—	—	Accepted value 1555° ± 2° C.
Cooling.....	$\left. \begin{matrix} 1555 \\ 1556 \\ 1553 \end{matrix} \right\}$ as summed	—	—	1539 : 2 : 2	—	—	—	
Mean	$\left. \begin{matrix} 1552 \\ 1558 \\ 1553 \\ 1559 \end{matrix} \right\}$	—	—	—	—	—	—	

Note.—The first figure given in the column is the melting or freezing point in degrees Centigrade. The second the number of determinations included in the average. The third is the total number of individual observations made during these determinations.

II.B. The Bubble Method.

During an attempt to measure the temperature of molten nickel by sighting on the liquid surface it was suggested by Dr. W. Rosenhain that a bubble blown in the liquid would be ideal black body.

The experimental difficulties in maintaining a bubble in a molten metal or alloy are, however, great, and again the success of this method depended to a large extent on the production of suitable refractory tubes. The bubble is not only to be blown but also to be maintained at the end of a tube which dips into the melt; this entails that the tube must be made of a refractory material which is not rapidly corroded by the liquid, but withstands a slight pressure of gas and does not bend or sag at the high temperatures reached during the experiment.

No hard alumina tubing was available when the research started and consequently tubes formed of silica, impure magnesite, soft alumina, "pythagoras masse" and china-clay containing 25 per cent. of alumina were used. This resulted in experimental difficulties which were later eliminated by the production of and the use of hard alumina tubing.

Since the varieties of tubes mentioned above were all found to react with the molten metal, the small refractory head B as shown in fig. 2 was used to keep the end of the pythagoras or china clay-alumina tubing, etc., out of contact with the hot molten metal.

A small hole, 2 mm. in diameter, was bored in the end of the tube C (see fig. 2) which dips into the molten liquid. The tubing A was then luted into the top part of the head B as shown in fig. 2. By these means the pressure of gas necessary to blow a bubble in the melt could be maintained and at the same time the tubing was kept out of contact with the molten metal.

Fig. 8 shows the general arrangement for blowing a bubble in the melt as well as the black body head and tube. In this method the pressure and therefore the position of the molten metal in the tube E is regulated by the depth of immersion of the blow-off tube inside B.

(i) *Iron*.—About 90 gm. of metal were placed in a 1-inch diameter alumina pot and melted down in an atmosphere of hydrogen. When molten, the tube E (fig. 8) which during heating has been held just above the melt, and down which gas is passing, is lowered into the melt until an immersion of approximately $\frac{1}{2}$ -inch is obtained. The pressure of gas is then adjusted so that a bubble just breaks away from the end of the control tube B. No actual examination of the size of the bubble blown in the melt was made; but from

the facts observed it is highly probable that the bubble must have been small and that it tends to be blown and to break on one side of the tube. On examination of the metal after it had become solid, only a very small bubble was found at the base of the tube, and in some cases slight convexing of the surface of the solid metal at the base of the tube suggested that the metal tends to rise up the tube on solidification possibly owing to ejection of gas on solidification. The results of these experiments are summed up in Table I, column 6.

The experiments by the bubble method were the earliest to give results agreeing with those which are regarded as the final values for iron. The values obtained for the melting point of iron were about 20° C. higher in the case of the bubble method than in the case of refractory tubes without baffle-plugs.

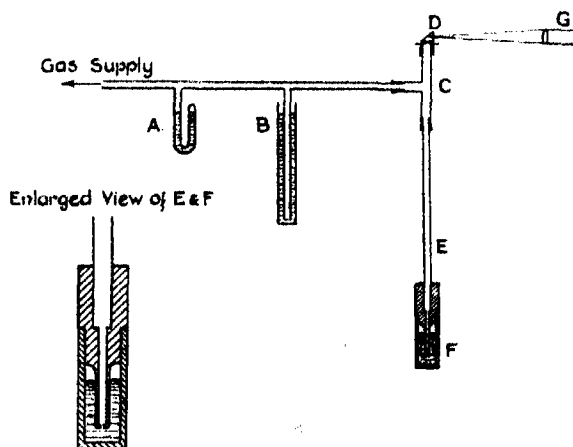


FIG. 8.—A. Manometer. B. Cylinder of water. C. Glass T-piece. D. Prism. E. Tube passing into black body head. F. Melt. G. Optical Pyrometer.

Using the above bubble method for determining the melting and freezing point of iron, the mean value obtained was 1528° C. This is 1° C. higher than that obtained by the methods using immersed refractory tubes as shown in Table I, columns 4, 5, 8, 9 and 10.

In the case of the determination of gold and palladium the bubble method did not give very satisfactory results.

(ii) *Gold*.—In the case of gold the internal surface of the bubble did not allow easy matching with the filament of the optical pyrometer. This method was tried, firstly, by forming a bubble at the end of the immersed tube without

allowing any excess of gas to escape there, and, secondly, by allowing excess of gas to blow off from the end of the tube.

In the first case the apparent temperature of the surface of the bubble was irregular; in addition to the irregularities dark patches were noticed which were probably due to reflections down the observation tube from outside. In this experiment 150 gm. of gold were used. After a repeat experiment on sectioning the solidified ingot, which weighed 500 gm., the depth of immersion of the tube was found to be 1.4 cm., but no spherical cavity had been formed. The base of the cavity consisted of a roughly horizontal surface which had shrunk somewhat from the tube. A free passage for the gas had been formed between the solid ingot and the outside of the tube; this was indicated by the cessation of bubbles at the end of the tube B.

In the second case it was noticed that if the stream of gas were increased and gas escaped through the liquid gold, the surface of the bubble appeared dark owing to reflection from the cold end of the observation tube; but if the pressure were then reduced so that gas did not blow off from the immersed tube the effects of reflection diminished until only a very small black area remained. During freezing the apparent temperature of the molten metal surface was not uniform. At the beginning of solidification the surface suddenly became relatively quite dark, bright areas then developed spreading over this surface until they completely covered it. This appearance then reversed until finally about one-quarter of the surface remained dark and the rest of varying brightness. The subsequent examination of the solidified ingot shows that the internal surface of the blown cavity becomes crinkled during solidification.

In addition to the difficulty just mentioned it is probable that metallic vapour may interfere especially when no gas is being blown through the immersed tube. The higher reflective power of the gold possibly tends to render the effect of the wrinkled surface very pronounced whereas in the case of iron the surface of the metal inside the cavity does not appear to be disturbed.

It is probable also that the density of the molten metal also determines the relative sizes of the bubbles blown. In the case of gold and iron, the former is nearly $2\frac{1}{2}$ times as dense, and hence the size of bubble in the solid ingot would tend to be less in the former than in the latter case.

In the case of iron satisfactory results were obtained although there was a very noticeable but small black spot in the bubble. This was produced, as in the case of gold, by reflection from the external surface down the tube, but the spot could be kept out of the matching area. By increasing the

quantity of gas the dark spot moved to one side and oscillated in position ; a still greater stream of gas caused the bubble to be of such a shape that no external light was reflected up the tube.

(iii) *Palladium*.---Experimental difficulties were found which appear to be caused by the tendency of this metal to absorb gases such as hydrogen and nitrogen and perhaps to attack the refractories.

The results obtained by the bubble method were 16° C. lower than those obtained by the squatting wire. It was found that considerable quantities of gas were evolved on solidification. The evolution occurred in such a manner that as the metal froze the last portions to remain liquid metal were forced up the central tube, even above the level of the ingot. Under these conditions the observations were not reliable as the black body enclosure formed in the molten metal was not maintained. Heating curve determinations could not, therefore, be made.

IIC. *Squatting Wire Method.*

The calibration of the optical pyrometer has been carried out at the palladium melting point by the "squatting wire" method which has been previously referred to on page 93. Table I, column 2, shows the values obtained for the melting point of palladium when the mean of the temperatures observed by the optical pyrometer was assumed to be 1555° C. This is the accepted value for the melting point of palladium. An attempt has been made to adopt this method in regard to iron, but owing to the reaction of the iron with the thermocouple wires, as described later, satisfactory temperature comparisons were not attainable. An auxiliary comparison has been effected by means of the rotating sector method which is referred to later.

Fig. 9 shows the arrangement of the apparatus for the "squatting wire"

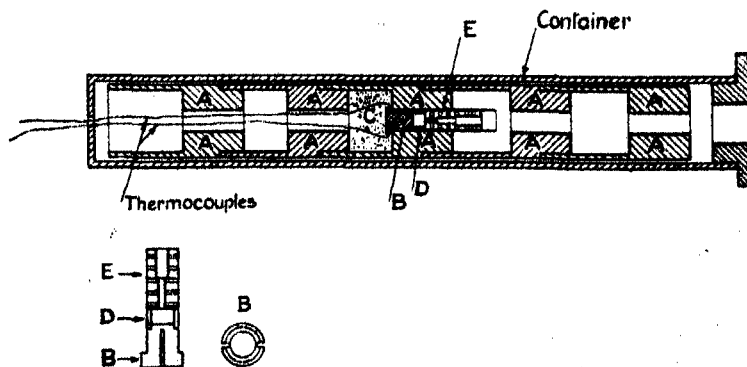


FIG. 9.

method. A series of large alumina pots (A) as shown in fig. 3 is arranged as shown in the diagram and the holes in their bases formed excellent diaphragms for obtaining black body conditions in a tube furnace. A stopper B, made from a hard alumina block is fitted into the end of the central tube of the middle pot; thermocouple wires are laid in slots cut on opposite sides of the stopper B. The palladium or iron bridge joining these wires rests on the end of the stopper B in the tube. The space C is filled with ground alumina which forms a hard cake so that the stopper B cannot move out of its position in the tube. On top of the plug B and fitting over the wires, a little cylindrical ring D of hard alumina is placed and above this a perforated hard alumina baffle-plug E, the central hole down which is tapered. The whole arrangement is placed in a glazed china clay container, the thermocouple wires passing out through a hole in the bottom, while the opposite open end of the container is used for observing the black body temperature of the wires across the stopper B. The whole is then placed in a tube furnace heated by six silit heating elements which uniformly heat a long length.

In the case of iron, thermocouple wires were bent tightly round the small holes at both ends of a strip of pure electrolytic iron. While the observations were taken, the temperature was raised at the rate of approximately 2° C. per minute.

No satisfactory value was obtained for the melting point of iron by this method, one reading being 34° C. lower than the ultimate value arrived at in this research. The above indicates that during the necessarily slow rate of heating, the platinum and platinum-alloy thermocouple wires probably alloy with the iron.

In one case it appeared highly probable that some—perhaps high melting—alloy had been formed during heating. Attempts were made to obtain satisfactory results using wires which would not react with the iron, such as thin tungsten-molybdenum couple wires in hydrogen, but wires of this thickness became brittle and broke during the experiment.

The results are given in Table I on p. 102.

III. Calibration of the Optical Pyrometer.

In order to calibrate the optical pyrometer over a suitable range of temperature, the "sector" method was adopted.

In this method, which has been fully described by previous investigators*

* Forsythe, 'Chemical and Metallurgical Engineering,' vol. 22, p. 1213 (1920); Fairchild, Hoover and Peters, *loc. cit.*; Schofield, *loc. cit.*

a sector, rotating at constant speed, is inserted between the optical pyrometer and the source of light. The light transmitted by the sector is only a small fraction of the amount emitted from the source and a sector of suitable dimension is selected so that the amount transmitted approximated to that radiated from a black body of known temperature. In the present instance the black body temperature of the melting point of gold has been taken as the standard and the actual temperatures of the unknown source, *i.e.*, the melting points of the metals in question, have been calculated by means of the following equation

$$\frac{1}{\theta_2} - \frac{1}{\theta_1} = \frac{\lambda \log R}{C_2 \log_{10} e}.$$

where θ_2 and θ_1 are the two absolute temperatures involved.

λ = the effective wave-length of the red filter used in the optical pyrometer.

R = the percentage transmission of the sector.

C_2 = the radiation constant which is taken as 1.432μ degrees for the purposes of the International Temperature Scale.*

The temperature of the melting and freezing of iron has been determined by this method as a standard material for future use. The intermediate temperatures between gold and iron were determined by observation of a black body at constant temperature.

The fusion temperatures obtained by calculation from the observed values are given in Table I, columns 4 and 9.

Melting Point of Iron.—The temperatures of the melting and freezing point of iron determined by the "sector" method and by sighting into an immersed refractory tube as shown in fig. 2 are 1529°C. and 1525°C. respectively, which give a mean value of 1527°C. Sighting into a tube formed in the base of the large crucible as shown in fig. 4 gives the corresponding values 1524°C. and 1530°C. The final value for the melting and freezing point of iron may, therefore, be taken as 1527°C.

The iron has been prepared electrolytically by deposition from a chloride solution and was melted *in vacuo* in an alumina crucible to remove the excess of oxide and to eliminate gases. This treatment was followed by several remeltings in a current of hydrogen until the oxide content was reduced to an

* "Comptes Rendus des Séances et Mesures" (Paris, 1927) (Sept. Conférence Générale des Poids).

amount such that the particles of oxide were only with difficulty detected under the microscope. In this condition the analysis of the material was as follows :

Carbon	= 0·005 to 0·017 per cent.
Silicon	Trace to 0·009 per cent.
Sulphur	Nil to 0·001 per cent.
Phosphorus	0·002 per cent.
Manganese	Trace.
Copper	Trace to 0·006 per cent.

The purity of the iron before remelting ranges therefore from 99·98 to 99·99 apart from the oxygen content.

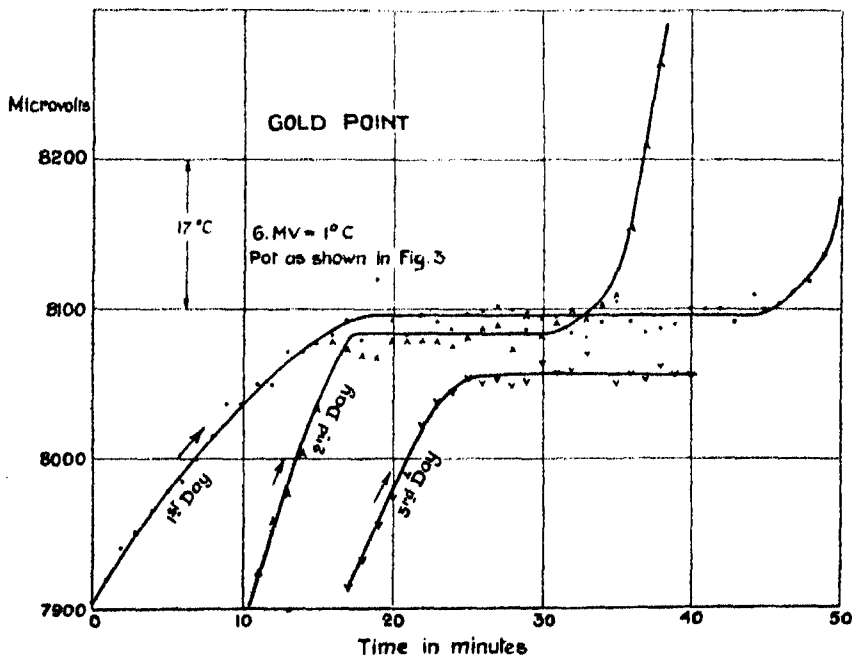


FIG. 10.

One of the ingots used in the melting point determination was analysed to confirm the maintenance of purity and the results are as follows :—

Carbon	= 0·010 per cent.
Silicon	0·030 per cent.
Sulphur	Trace.
Phosphorus	0·014 per cent.
Manganese	Trace.
Oxygen	0·05 per cent.

It appears that an increase in the silicon content has occurred; this has been confirmed in a second ingot. It seems probable that hydrogen is responsible for both the reduction of some of the siliceous material in the muffle and also the transference of a little of the resulting silicon to the molten iron.

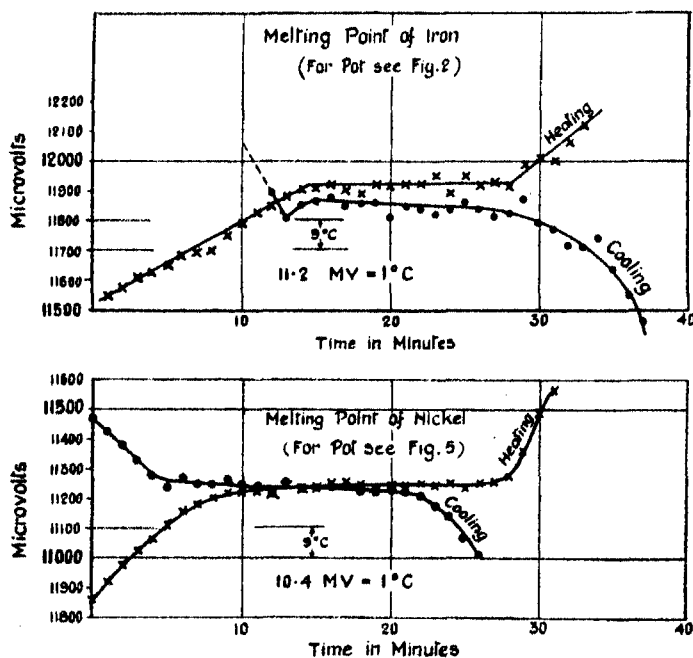


FIG. 11.

The principal previous determinations of the melting point of iron have been considered in relation to the present value $1527^{\circ} \pm 3^{\circ} \text{C}$. The results are contained in Table II. on p. 111.

In the above determinations the temperatures have been measured by immersing a thermocouple in the molten metal. Burgess and Waltenburg, using an optical pyrometer, also observed the temperature at which small pieces of iron were found to lose their shape on melting. The reference points or fundamentals of the temperature scale have not in all cases been given, but in one or two instances, where the means of calibration of the thermocouple has been given, the melting point of iron is higher than the calibration temperature.

The determination of the thermal changes in solid metals or alloys involves several considerations. The methods are similar to those adopted in regard to the use of the thermocouple but owing to the difficulty of matching the

Table II.

Investigators.*	M.P. of iron, °C.	Based upon M.P. of palladium °C.	Impurities reported in the iron, per cent. by weight.
Carpenter and Keeling†	1505	—	C = 0.01; P = 0.04.
Isaac and Tamman	1524-7	—	C = 0.07; Si = 0.09; Mn = 0.08. P = 0.01; S = 0.015; Cu = 0.023.
Burgess and Waltenburg	1530 ± 5	1549	C = 0.00-0.012; Si = 0.00-0.013. P = 0.00-0.007; Cu = 0.008. S = 0.00-0.004; Mn = 0.00.
Ruer and Klesper	1528	—	C = 0.009; Cu = 0.03. S = 0.001-0.002.
Tritton and Hanson‡	1535 ± 5	1555	C = trace; O ₂ = 0.08.
Andrews	1537	—	Decarburised armco iron.

* Carpenter and Keeling, *J. I. & S.I.*, vol. 65, p. 242 (1904); Isaac and Tamman, *Z. Anorg. Chem.*, vol. 53, p. 281 (1907), and vol. 55, p. 58 (1907); Burgess and Waltenburg, *Bull. Bureau of Standards*, vol. 10, p. 89 (1914); Ruer and Klesper, *Ferrum*, vol. 11, p. 257 (1914), and vol. 13, p. 1 (1916); Tritton and Hanson, *J. I. & S.I.*, vol. 110, pp. 2, 100 (1924); Andrews, *J. I. & S.I.*, vol. 119, pp. 1, 330 (1929).

† In regard to the determination of Carpenter and Keeling, the value 1505° C. is based upon a melting point of platinum given as 1710 ± 5° C. More recent determinations place this point from 45-65° C. higher than the value accepted at that time as a result of extrapolation of the thermocouple calibration scale from about 1000° C. A comparison of the thermocouple with the nitrogen thermometer had been made at 1000° C. by Dr. J. H. Harker.‡ The value given by Carpenter and Keeling is thus probably raised 20-30° C. from 1505° C. This addition can also be made to the value of the melting point of nickel which was stated by Harker§ to be 1427 ± 3° C. and is now accepted to be at 1451° C.

‡ The value given by Tritton and Hanson was the end point of the liquidus of a binary constitutional diagram of the alloys of iron and oxygen and was used to correlate the results with that of the melting point of palladium.

§ Harker, *Proc. Roy. Soc., A*, vol. 76, p. 247.

filament, as previously mentioned, it is desirable to use observations of the temperature at constant intervals of time during the period of heating or cooling the alloy. This prevents the use of the plotting chronograph by which the time intervals for definite increments or decrements in temperature can readily be plotted as a curve, and it is, therefore, preferable to plot the data by means of direct time-temperature curves.

From the experience gathered it would appear that where no particular corrosive or volatile element is present it is generally preferable to use the thermocouple method until temperatures are reached at which it is becoming difficult to maintain platinum alloy thermocouples to their calibration possibly at 1450-1550° C.

The procedure in regard to the melting points of alloys is similar to that of

the pure metals. The rate of cooling the furnace containing the alloy under examination must be considerably slower in the case of the optical method than that permissible with a thermocouple. A rate as low as 1° to 2° C. per minute is found to give satisfactory results whereas rates of cooling as high as 3° to 8° C. have sometimes been adopted in respect of thermocouples.

Examples of the data obtained by the present optical method are shown in fig. 12. The two sets of curves show the data relating to two alloys from the

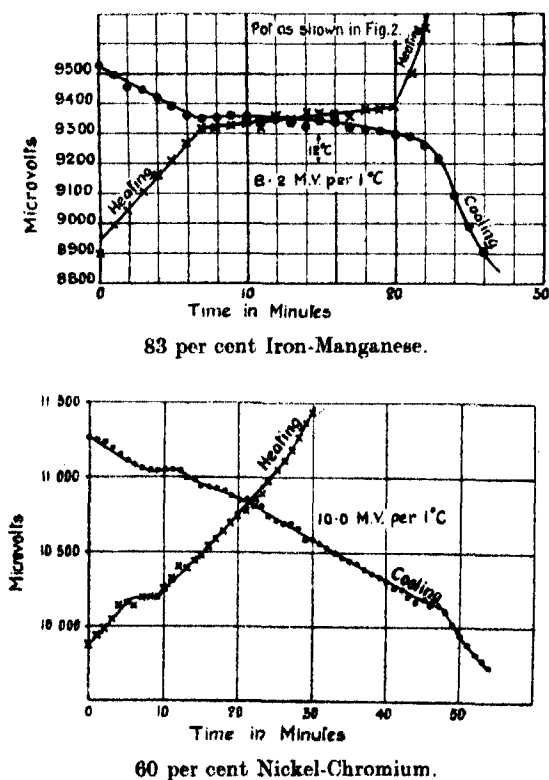
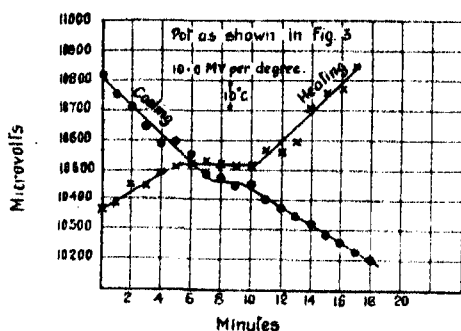


FIG. 12.

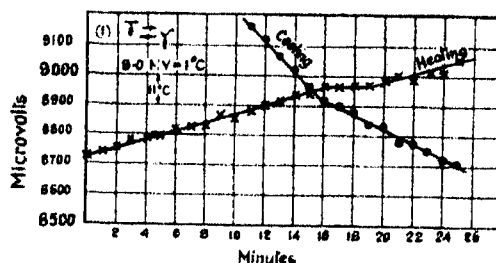
binary systems iron-manganese and nickel-chromium. These examples show respectively the commencement of solidification and the subsequent thermal changes.

To test the usefulness of the present method for the study of alloys in the solid state, a determination of the already known critical change points in iron and manganese has been undertaken. Observations were made in the latter case by sighting into the metal through a hole bored at the bottom of the tube already embedded in the ingot from a previous melting point determina-

tion; in the case of iron a hole drilled in the solid ingot was used. The results are given in figs. 13 and 14.



δ to γ Transformation in Iron.



Transformation in Manganese.

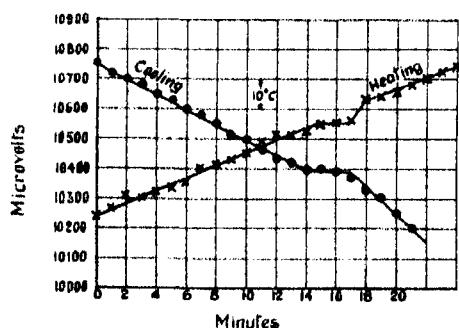


FIG. 13.

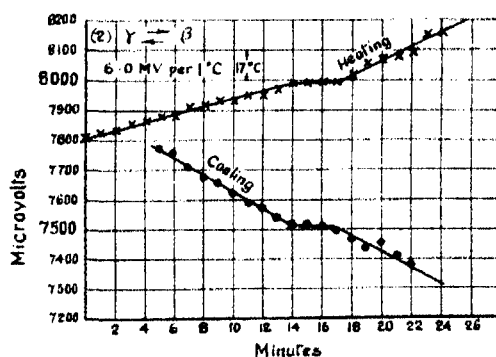


FIG. 14.

A further example of the use of the method at about 700°C . is given in fig. 15. This diagram indicates the thermal changes in a steel containing 0.65 per cent. of carbon.

General Summary.

1. The paper describes the adaptation of the optical pyrometer to the determination of melting, freezing and transformation temperatures in metals and alloys by observation of a "black body" enclosure immersed in the metal. The observations, which are taken at regular time intervals, are plotted in the usual form of thermal curves, preferably of the "time-temperature" type.

2. Refractory containers in hard pure alumina have been prepared. The crucibles and the method of production are described and also the precautions necessary to ensure satisfactory black body conditions.

3. The "bubble method" previously described by Dr. W. Rosenhain has been used successfully in the determination of the melting point of iron.

4. The calibration of the optical pyrometer has been carried out by means of the melting points of gold and palladium and intermediate temperatures by comparison with thermocouples. The use of the rotating sector has confirmed the shape of the calibration curve. The melting point of gold has been taken to be 1063°C . and palladium $1555^{\circ} \pm 2^{\circ}\text{C}$. In the case of iron, the rotating sector method has confirmed the new value of the melting point obtained in reference to the melting point of palladium during the course of this investigation.

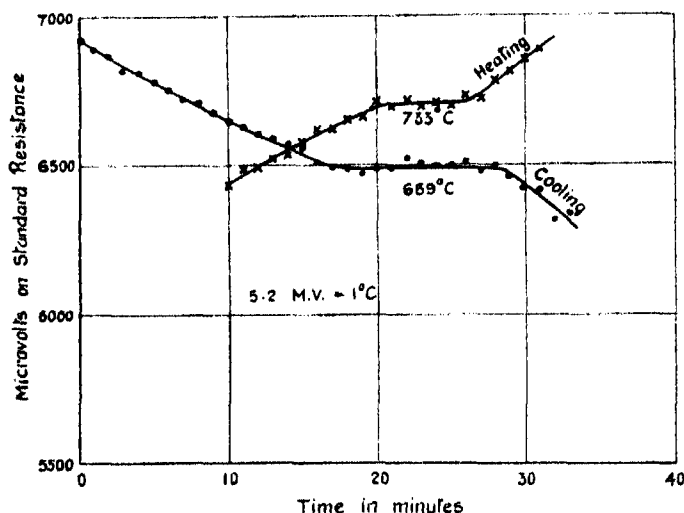


FIG. 15.

5. The method has been found suitable for melting point determinations of alloys at high temperatures, but existing thermocouple methods appear preferable for the determination of the transformations in metals and alloys at lower temperatures.

6. The effect of metal vapour has been described and a method for counteracting the absorption of light from this cause has been developed.

7. The melting point of iron of very high purity has been determined and referred to the generally accepted melting point of palladium at $1555^{\circ} \pm 2^{\circ}\text{C}$., has been found to be $1527^{\circ} \pm 3^{\circ}\text{C}$.

The authors desire to thank Dr. W. Rosenhain, F.R.S., for his continued interest and encouragement during the stages of progress of the research. They wish to acknowledge the able assistance of Mr. R. P. Garner and Mr. H. Grant in the experimental side of the research.

*An Experimental Investigation of the Flow behind Circular
Cylinders in Channels of Different Breadths.*

By L. ROSENHEAD, Ph.D., St. John's College, Cambridge, with an APPENDIX
by M. SCHWABE, Kaiser Wilhelm-Institut für Strömungsforschung,
Göttingen.

(Communicated by H. Jeffreys, F.R.S.—Received May 12, 1930.)

[PLATES 9, 10.]

1. *Introduction.*

The general characteristics of two-dimensional flow behind a cylinder of any cross section are well known, and for the purposes of mathematical investigation it has been assumed that at an appreciable distance from the obstacle, the vortices in the wake assume a regular formation known as the "unsymmetrical double row" or "Karmanstrasse"—in which each vortex is opposite the mid-point of the interval between consecutive vortices on the other row. The form of the wake seen experimentally justifies, in some measure, the adoption of this assumption. The theoretical investigation of the stability of such double rows in a channel* brought out some unexpected results and it was thought that an experimental investigation would throw some light on the subject. Quite a number of experimenters have, from time to time, investigated the two-dimensional flow behind a cylinder, but there has been no systematic attempt to find the effect of the channel walls on the dimensions of the Karmanstreet. Further, the existence of some possible simple functional relation between the various dimensions has almost always been masked by the choice of an obstacle of complicated cross section, the most usual obstacle being one of aerofoil section. It was therefore thought advisable to use some cylinder of circular section so as to avoid, to some degree, the complications introduced by the shape of the obstacle. No theoretical explanation of the results is attempted, but the figures derived from the investigations are submitted as information on various features of the flow.

The actual experiments were conducted by Herr M. Schwabe at the Kaiser Wilhelm-Institut für Strömungsforschung, at Göttingen, and it was his patient investigation that made it possible to obtain a complete description of the vortex motion. Figs. 1-6 of this paper, and part of the tables, were

* 'Phil. Trans.,' A, vol. 228, p. 275 (1929).

completed by him at Göttingen. I feel extremely grateful to him for having undertaken the investigations and for having carried them out in such an efficient manner. My thanks are also due to Prof. L. Prandtl, Director of the Kaiser Wilhelm-Institut, for having allowed the experiments to be conducted in his laboratory and for having put at my disposal the apparatus and facilities which made the experiments possible. In the last instance, however, my thanks are due to the Department of Scientific and Industrial Research whose Senior Research Award enabled me to finance the investigations.

The experiments were begun in November, 1929. The description of the experimental side of the investigations has been left to Herr Schwabe, and his remarks are attached to this paper in the form of an Appendix. A certain amount of description of the experimental side is necessary here however before the results are given, but the overlapping has been reduced to a minimum. A tank of length 60 cm., width 20 cm., and depth 13 cm. was used. The tank had movable walls which could be placed at distances of 16·8, 10·2, 5·2, 3·0 cm. from each other. The obstacles used were two cylinders of circular cross section, the diameters being 1 cm. and 2 cm. respectively. The cylinders were pushed through the water in the channel with velocities ranging from 0·5 to 11·5 cm. per second. The surface of the water was lightly strewn with aluminium powder and the system was illuminated from above. The wake was photographed from above by means of a continuously recording roll-film apparatus which was at rest relative to the tank. The films were enlarged, positives were made and measurements were taken. The paths of the vortices were obtained as explained in the Appendix, and the velocities of the vortices in certain relevant cases were also determined. The Reynolds number $R = 2lV/\nu$ (where $2l$ is the diameter of the cylinder, V the velocity of the cylinder, and ν the kinematic viscosity of the liquid) assumed various values between 20 and 1000.

In the theoretical investigation (*loc. cit.*) the wake was supposed to consist of two rows of vortices of equal strength, with positive vorticity on one row and negative vorticity on the other row. The distance between the two rows was $2a$, the distance between consecutive vortices on the same row $2b$, and that between the channel walls $2c$. The stream line forms were investigated and various diagrams were given. The stability of the system was investigated and it was found that the stability ratio a/b was only determinate when the distance between the rows was less than 0·208 of the distance between the channel walls. If a/c was greater than 0·208 then there was a range of values that could be assumed by a/b . On general principles, however, we know that

$a/b = f(R, l/c)$, and as we are dealing with a perfect fluid, $R = \infty$, and we should expect that $a/b = \phi(l/c)$ which gives a unique value for a/b for each value of c . The result obtained from the stability investigations therefore contradicts what one might expect from a consideration of general principles, and this point lends additional interest to the experimental results.

Relf has published curves which show, in effect, the variation with increasing Reynolds numbers, of the drag-coefficient of,* and the frequency of the shedding of vortices behind,† cylinders of circular section in an unbounded medium. This paper supplements these publications in that it gives curves which show the variation of other characteristics of the flow with varying Reynolds numbers and varying values of the ratio of radius of cylinder to width of channel.

2. List of Symbols.

- κ = strength of a vortex.
- $2a$ = distance between the vortex rows in centimetres.
- $2b$ = distance between consecutive vortices on the same row in centimetres.
- $2c$ = distance between channel walls in centimetres.
- $2l$ = diameter of cylinder in centimetres.
- μ, ρ, ν = viscosity, density, kinematic viscosity ($= \mu/\rho$) of the liquid.
- R = Reynolds number $= 2lV/\nu$.
- V = velocity of the cylinder in centimetres per second.
- V_1 = velocity of the vortices in centimetres per second.
- T_0 = temperature of the liquid in degrees centigrade.
- B = exposure time of the film in seconds.
- n = number of exposures per second.
- l = time from beginning of motion of cylinder to middle of exposure of film in seconds (see Table II).
- m = distance travelled by cylinder from beginning of motion to middle of exposure of film in centimetres (see Table II).

In figs. 7, 9, 10, 11, the points marked $\times$, $\odot$, ϕ , Δ , $\square$, belong to the curves. $l/c = 10/15, 10/30, 10/52, 10/102, 10/168$ respectively.

3. The Stream Line Forms.

It is generally known that for small velocities of the cylinder no vortices are shed, and that for large velocities of the cylinder the vortices formed

* 'R. & M.,' No. 102, Adv. Ctte. for Aeronautics, 48 (1913-14).

† 'Phil. Mag.,' vol. 42, p. 175 (1921).

diffuse so rapidly that it is impossible to speak of the formation of a double row. The latter phenomenon manifests itself most strongly when the channel is narrow. These points are verified by the experiments and it is found that the vortices are only shed when the velocity of the cylinder lies within the range 0.5 to 7.0 cm. per second. Another point which diminishes the range within which one can speak of the formation of a double row is the fact that the water in the tank possesses a free surface and that at high speeds, large surface waves are produced and these give rise to a three-dimensional motion in the channel which quickly causes the vorticity to diffuse. However, the stream line forms that are seen are quite sufficient to verify, qualitatively, the results obtained from the theoretical investigations. Bénard,* Karman,† and others have at various times published pictures which bear a marked resemblance to the diagrams referred to above, but they are in the most part isolated examples which were not given to demonstrate any particular point. The following sequence of photographs gives the shapes of the stream lines in various cases, and shows that the agreement between theory and experiment is quite good over the whole range in which the Karman street exists. Not all the pictures show wakes which are as regular as those given below and, as a matter of fact, Herr Schwabe remarks that experiments conducted under seemingly similar conditions give rise to wakes which may or may not be similar. This apparent anomaly is really easily explicable, if one takes account of the fact that the double row of vortices is unstable to three-dimensional disturbances.‡ This accounts in part for the fact that when the velocity of the cylinder is large the vortices diffuse rapidly owing to the existence of a three-dimensional motion in the tank. Further, even when the velocity of the cylinder is "reasonable" there exists some small three-dimensional motion, and any deviation of a vortex from the rectilinear form is magnified as the vortex travels downstream on account of the instability of the system to three-dimensional disturbances. Hence, small initial differences in the shape of the vortices will be magnified by distortion as the vortex moves along the wake, and thus the form of the wake in experiments conducted under exactly similar conditions may differ, at times quite considerably. This fact does not diminish the importance of those cases in which the vortices come off regularly, for here we see an approximation to the state in which the vortices are shed perfectly rectilinearly.

* 'C. R.' vol. 147, p. 839 (1908).

† 'Phys. Z.' vol. 13, p. 53 (1912).

‡ "The Spread of Vorticity in the Wake behind a Cylinder," 'Proc. Roy. Soc.,' A, vol. 127, p. 590 (1930).

In this latter case there is no instability—or rather, there may be an instability which in any case needs a fairly long time to make itself apparent. The dimensions of the street here approximate to those of the ideal two-dimensional motion without the distorting three-dimensional disturbance, and therefore are of importance.

There is an arrow at the top of each Plate which indicates the direction of motion of the cylinder. Each picture has a reference consisting of an index number and a subscript which relate the picture with the various tables. The following example explains the method. The second reproduction is marked 43₂. The index number 43 gives the number of the experiment and by reference to Table I we see that the experiment was done with cylinder 2 (of diameter 2 cm.), that the channel walls were 3.0 cm. apart, that the velocity of the cylinder was 2.17 cm. per second and that the Reynolds number was 386. The subscript 2 means that this was the second of those negatives of film 43 that were enlarged. The subscript 2 refers to Table II, in the third column of which we find the number 43₂. This negative was the twentieth on the film (see column 2 of Table II) and we see that the cylinder had been in motion for 15.2 seconds and had travelled a distance 31.2 cm. when this particular piece of film was exposed. Table I gives the time of exposure of the film and this accounts for the fact that the obstacle is seen as a blur.

Fig. 1 (Plate 9) shows two vortices coming off symmetrically, and fig. 2 shows another example of this type. The disturbing effects in the case shown by fig. 2 must have been very small, for in addition to the pair of vortices which are coming off symmetrically, there are two other pairs of symmetrically placed vortices immediately behind it. Fig. 3 is an example of a regularly spaced Karman street. Fig. 4 is an example of a regular wake at a distance of about 50 diameters from the cylinder. Fig. 5 (Plate 10) shows several phenomena rather clearly. The turbulent region just behind the obstacle is noticeable, as also the tendency to regularity which manifests itself in the middle of the picture. At the extreme right, however, the instability effect is seen to be growing. Fig. 6 shows some of the forms of stream lines that were obtained theoretically. On the left we see those forms that Bénard (*loc. cit.*) found experimentally and described as having "une forme de raquette." A little further to the right the form changes and the vortices appear to cling to the channel walls. Still further to the right the vortices have died out completely.

Table I.

Expt. No.	Cyl. No.	2c.	l/c.	V.	B.	n.	T _g .	ν .	R.	V _r .	V _i (mean).	V _i /V.	a/l.	a/c.	b/l.	a/b.
1	1	16.8	0.060	0.55	1.40	0.72	12.3	0.0123	45	0.045-0.060	0.053	0.05	1.8	0.108	5.4	0.33
2				1.05	1.60	0.52	12.3	0.0123	82	0.216-0.274	0.215	0.12			4.8	
3				2.00	0.64	1.44	12.3	0.0123	156	0.226-0.318	0.272	0.13			4.8	
4				2.13	1.50	0.62	12.5	0.0122	175							
5				9.00	0.60	1.60	12.6	0.0122	739							
6				9.70	0.30	3.06	12.6	0.0122	796							
7	1	10.2	0.098	7.50	0.35	2.60	12.2	0.0123	610							
8				3.90	0.75	1.23	12.2	0.0123	318							
9				2.05	2.00	0.45	12.4	0.0122	167	0.063-0.085	0.078	0.08	1.6	0.157	4.6	0.34
10				0.96	2.71	0.34	12.3	0.0123	78				2.6	0.255	5.6	0.46
11				0.50			12.2	0.0123	41							
12				0.29			12.4	0.0122	24							
13	1	5.2	0.192	0.29			12.5	0.0122	24	0.037-0.040	0.037	0.06	1.8	0.345	5.4	0.33
14				0.60	3.78	0.25	12.5	0.0122	49	0.043-0.060	0.052	0.05	1.4	0.269	4.5	0.31
15				1.10	2.00	0.45	12.5	0.0122	90	0.231-0.263	0.247	0.12	1.4	0.269	4.4	0.32
16				2.05	1.50	0.63	12.5	0.0122	168							
17				4.30	0.80	1.04	12.5	0.0122	352							
18				10.00			12.5	0.0122	820							
19	1	3.0	0.333	10.00	0.33	2.30	11.2	0.0126	792	0.555-1.000	0.740	0.18	1.2	0.400	3.6	0.33
20				4.10	0.68	1.32	11.2	0.0126	325	0.190-0.320	0.285	0.13	1.2	0.400	3.6	0.33
21				2.20	2.00	0.43	11.3	0.0126	175	0.195-0.217	0.206	0.16	1.2	0.400	3.6	0.33
22				1.29	3.20	0.30	13.7	0.0118	109							
23				0.60	4.20	0.21	13.7	0.0118	51							
24				0.68	4.20	0.21	12.5	0.0122	56							
25	2	3.0	0.667	0.61	4.60	0.20	12.3	0.0123	50	0.515-0.636	0.576	0.46	0.9	0.600	2.0	0.45
26				1.25	2.60	0.36	12.2	0.0123	102							
27				2.40	1.62	0.57	12.2	0.0123	195							
28				1.01	1.22	0.73	11.8	0.0124	81							
29				3.70	0.76	1.20	11.8	0.0124	298							
30				9.60	0.45	2.05	11.8	0.0124	772							

Table II.

Film No.	Negative No.	Index No.	<i>l</i> .	<i>m</i> .	Film No.	Negative No.	Index No.	<i>l</i> .	<i>m</i> .
1	42	1 ₁			21	5	21 ₁	14.8	29.9
2	18	2 ₁	33.0	34.0		7	21 ₂	19.5	40.7
	22	2 ₂	43.1	43.5		8	21 ₃	21.8	46.1
	27	2 ₃	54.1	54.9		9	21 ₄	24.2	51.5
3	25	3 ₁	17.8	32.7		10	21 ₅	26.5	58.8
	30	3 ₂	21.3	39.7	22	9	22 ₁	24.5	29.3
	35	3 ₃	24.7	46.7		11	22 ₂	30.1	27.6
	40	3 ₄	28.0	53.7		13	22 ₃	36.5	44.0
4	10	4 ₁	16.1	32.2		15	22 ₄	40.7	51.5
	15	4 ₂	24.1	45.7		17	22 ₅	46.1	58.9
9	8	9 ₁	16.3	33.2	23	13	23 ₁		
	11	9 ₂	22.6	46.0	24	11	24 ₁	49.9	32.7
	14	9 ₃	28.9	58.7		14	24 ₂	63.7	42.3
	17	9 ₄	34.9	70.7	25	11	25 ₁	54.9	32.6
	20	9 ₅	40.5	82.7	26	10	26 ₁	27.5	32.2
10	12	10 ₁	34.6	33.2		11	26 ₂	30.3	35.7
	15	10 ₂	43.4	41.7	27	8	27 ₁	12.7	28.4
	18	10 ₃	52.2	50.1		10	27 ₂	16.1	36.7
11	15	11 ₁				12	27 ₃	19.5	45.0
12	20	12 ₁			28	36	28 ₁	21.9	21.1
13	12	13 ₁				45	28 ₂	33.0	32.5
14	12	14 ₁	50.6	31.9	29	12	29 ₁	10.0	33.5
	15	14 ₂	62.9	39.3	30	10	30 ₁	4.7	36.0
	20	14 ₃	83.4	51.6	33	14	33 ₁	9.6	37.0
15	15	15 ₁	31.0	33.5	34	13	34 ₁	36.5	
	19	15 ₂	39.6	43.7		15	34 ₂	41.1	35.3
	23	15 ₃	48.2	53.0		17	34 ₃	47.7	40.9
	27	15 ₄	56.4	62.5		19	34 ₄	53.3	46.5
	35	15 ₅	72.8	82.7		21	34 ₅	58.8	52.1
16	11	16 ₁	15.9	33.0		23	34 ₆	64.3	57.6
	16	16 ₂	23.6	48.6		25	34 ₇	69.8	68.6
	19	16 ₃	28.2	57.9		29	34 ₈	80.7	79.5
	23	16 ₄	34.3	70.2	35	10	35 ₁	64.0	32.5
17	12	17 ₁				12	35 ₂	76.6	39.3
18	12	18 ₁				14	35 ₃	89.1	46.1
19	9	19 ₁			36	12	36 ₁	46.1	33.3
20	12	20 ₁	8.8	34.3		14	36 ₂	54.0	39.2
	14	20 ₂	10.2	40.3		16	36 ₃	61.7	44.8
	18	20 ₃	13.2	50.5		18	36 ₄	69.4	50.6
	22	20 ₄	16.2	60.5		20	36 ₅	77.2	56.4

Table II—(continued).

Film No.	Negative No.	Index No.	<i>l.</i>	<i>m.</i>	Film No.	Negative No.	Index No.	<i>l.</i>	<i>m.</i>
37	13	37 ₁	31.0	34.8	43	13	43 ₁	9.9	19.6
	19	37 ₂	45.7	51.9		20	43 ₂	15.2	31.2
	24	37 ₃	57.9	66.2		21	43 ₃	15.9	32.8
40	15	40 ₁	9.0	35.7		22	43 ₄	16.7	34.4
	20	40 ₂	12.1	49.2		23	43 ₅	17.4	35.9
41	11	41 ₁	15.6	33.5		26	43 ₆	19.5	40.6
	14	41 ₂	20.0	43.1		28	43 ₇	21.0	43.6
	17	41 ₃	24.4	52.7	44	14	44 ₁	20.1	22.3
42	17	42 ₁	6.4	23.6		18	44 ₂	25.5	28.9
	23	42 ₂	8.4	33.6		19	44 ₃	26.9	30.4
	26	42 ₃	9.7	38.1		20	44 ₄	28.1	31.9
						25	44 ₅	34.9	39.7
						26	44 ₆	36.2	41.1

4. *The Velocities of the Vortices.*

The paths and velocities of the vortices were determined by projecting the film negatives on to a table which was covered by a paper marked out in squares of 1 mm. side. The alteration in position of the vortices from film to film in relation to some reference line, was easily visible, and as this was combined with the known time of exposure of the film, the velocities were determined quite simply. These determinations are of course subject to some error. The twelfth column of Table I gives the velocities of the vortices. Those figures which are put in column eleven of this table give the upper and lower limits of the vortex velocity. No determinations were attempted in the cases where the spaces are left blank, either because no vortices were being shed or because the motion was very irregular. Column thirteen of Table I gives the ratio V_1/V as determined. The probable error in these determinations were taken into account when a smooth curve was drawn through the results (see fig. 7). The ordinate in this figure is V_1/V where V_1 is the velocity of the vortices and V that of the cylinder; the abscissa is the Reynolds number. Firstly, we grouped together all those determinations which had the same value of l/c . There are five such groups corresponding to the $l/c = 10/15, 10/30, 10/52, 10/102, 10/168$ respectively. Through each of these groups a smooth curve was drawn. As might be expected many of the determinations do not lie on a smooth curve. The greatest regularity in the velocity is apparent in the case where the channel is widest, that is $l/c = 10/168$, and the points do not deviate very much from the mean curve. In drawing the curves through

the other groups of points, reference was made to the probable error of each determination. Where the range of possible values of V_1/V was small, the curve was drawn to pass through or very near the mean point. Where the range was large and where not much importance could be attached to the mean value, the curve was drawn so as to pass through the range and to fit in with the other determinations. The result is the set of five curves shown in fig. 7. Of these curves the one corresponding to $l/c = 10/168$ may be taken as the most accurate, and the others give the general order of the value V_1/V for given values of l/c and R .

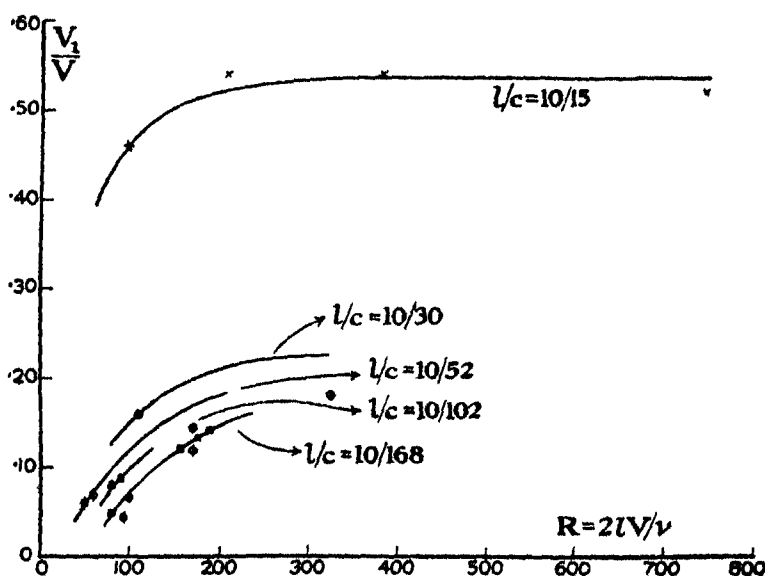


FIG. 7.—The ordinate is the ratio of vortex velocity to cylinder velocity. The abscissa is the Reynolds number. The value l/c gives the ratio of the diameter of the cylinder to the width of the channel. For further explanation see paragraphs 2 and 4.

Heisenberg's analysis* for the wake behind a flat plate leads to the result that $V_1/V = 0.229$ in an unbounded perfect fluid. The case $l/c = 10/168$ is our nearest approximation to the limiting case of the wake behind a circular cylinder and we see that at high Reynolds numbers, by a rough extrapolation, $V_1/V = 0.225$. This does not agree very well with the determinations of Karman who found that $V_1/V = 0.14$ for a circular cylinder, and $V_1/V = 0.20$ for a flat plate. One feature that is brought out by the curves in fig. 7 is the sudden increase in the value of V_1/V as l/c becomes comparable with unity.

* 'Phys. Z.', vol. 23, p. 363 (1922).

The increase between 10/15 and 10/30 is about 10 times that between 10/30 and 10/52.

5. *The Paths of the Vortices.*

The paths of the vortices show curious similarities and dissimilarities and they have been divided into four groups, representatives of which are given in fig. 8. In the first of these groups (experiments 2, 10, 14, 36) the velocity

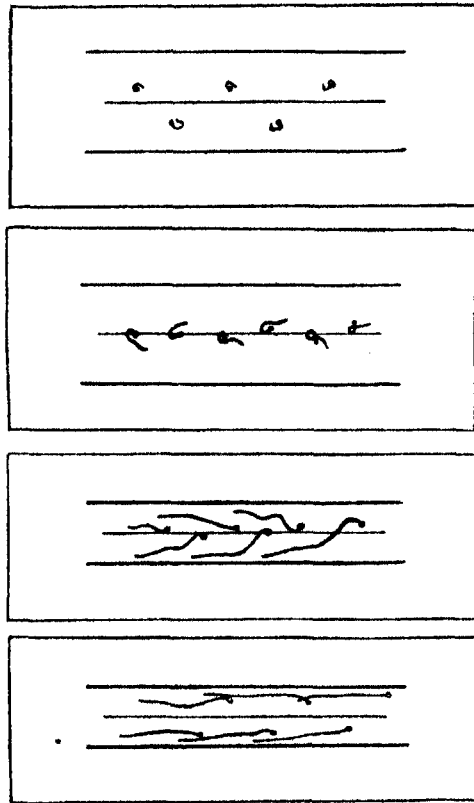


FIG. 8.

of the vortices is small but fairly constant. In the second group (experiments 3, 4, 15, 34, 41), the initial motion of the vortices seems to be towards the axis of the channel and away from the cylinder. This state of affairs only continues for a very short period, after which they follow the cylinder and at the same time spread out towards the walls of the channel. The velocity of the vortices first decreases and attains a small minimum; it then increases rapidly and attains a fairly constant, or slowly increasing, value. In the third

group (experiments 16, 20, 21), the initial motion away from the cylinder is lost, but the initial motion towards the centre of the channel, with a diminution in the value of the velocity, is quite apparent. The vortices then move quickly towards the walls of the channel and follow the cylinder with an increased velocity. In the fourth group (experiments 22, 26, 28, 42, 44), both the components of the above initial motion are lost and the vortices follow the cylinder with a fairly constant velocity in straight lines or in paths which are only slightly curved. In the majority of cases, however, the vortices develop a tendency to spread away from the axis of the channel, and this is taken as additional evidence in favour of the view that the Karman street is in reality unstable.

6. *The Spacing of the Vortices.*

There are two points of interest here—the longitudinal spacing of the vortices and the distance between the rows. One of the features of the flow that is least subject to variation is the constancy of the longitudinal spacing of the vortices. This demonstrates that the rate of generation of vorticity in each experiment is constant. In almost every experiment, no matter how irregular the configuration of the vortices, the horizontal distance between consecutive vortices remained nearly constant for that experiment. This remained approximately true even when instability manifested itself and the vortices meandered away from the axis of the channel, the mechanism of the motion being something as follows. When the vortices have passed through the turbulent region just behind the cylinder, the major influence determining the motion, such as the velocities induced by neighbouring vortices, tend to regularise the configuration and generate a constant horizontal velocity. This tendency is noticeable in almost every experiment. Meanwhile the instability effect increases with time and induces additional velocities both in the direction of motion and perpendicularly to it. The induced velocity in the direction of motion is small at first, and is masked by the comparatively large velocity of the vortices. The induced velocity perpendicular to the axis of the channel, however, is not masked and manifests itself by a motion of the vortex towards the walls of channel. This does not affect to any great measure, at first, the constancy of the longitudinal velocity of the vortices and the horizontal spacing of the vortices. Ultimately, however, the destabilising effect dominates and at the tail ends of rather long wakes the horizontal spacing is seen to change, in some cases decreasing and in others increasing. The ultimate decrease in the horizontal spacing is most apparent when the distance between the rows

is large in comparison with the width of the channel, in which case the vortices tend to cling to the walls. The relation between the two ratios (b/l) and (l/c) as R varies is shown in fig. 9.

For small values of the Reynolds number there appears to be a tendency for (b/l) to increase rapidly, but for the greater part of the range the ratio (b/l) has a constant value and appears to be independent of the Reynolds number. Heisenberg's analysis (*loc. cit.*) for a wake behind a flat plate yielded the result $b/l = 5.5$. These investigations deal with the wake behind a cylinder,

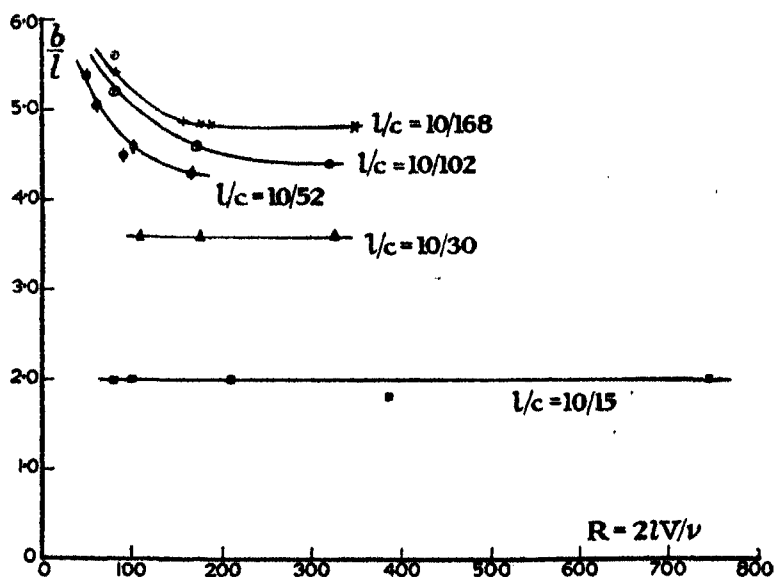


FIG. 9.—The ordinate in this figure is the ratio of the horizontal spacing between consecutive vortices on the same row to the diameter of the cylinder. The abscissa is the Reynolds number. The value l/c gives the ratio of the diameter of the cylinder to the width of the channel. For further explanation, see paragraphs 2 and 6.

but neglecting this difference for the moment, we see that our nearest approximation to the ideal case is the group of experiments in which $l/c = 10/168$, and in this case we see that for large values of the Reynolds number $b/l = 4.8$. Karman found that b/l for a flat plate was 5.5, and that for a circular cylinder $b/l = 4.3$. (In comparing our experimental results with the theoretical ones of Heisenberg it should be remembered that his investigations are based on the supposition that the vortex system is stable to two-dimensional disturbances.)

The determination of the distance between the rows showed that the constancy of a only became noticeably evident when the channel was narrow.

The walls seemed to impress a regularity on to the vortices, and although the wake in these cases were of comparatively short length, they were fairly uniform. When the walls were wide the trails of vortices were longer, but they were more irregular in that the vortices were always moving away from the central line and it was impossible to determine the correct mean value for a . This agrees with the experimental evidence of Fage and Johansen* who say definitely that the vortices do not flow along in parallel rows. In certain cases, however, there were sequences of some eight to ten vortices which showed a regularity of configuration, and after them the other vortices became distorted. The dimensions of the regular part of the pattern were taken as those of the ideal undistorted system.

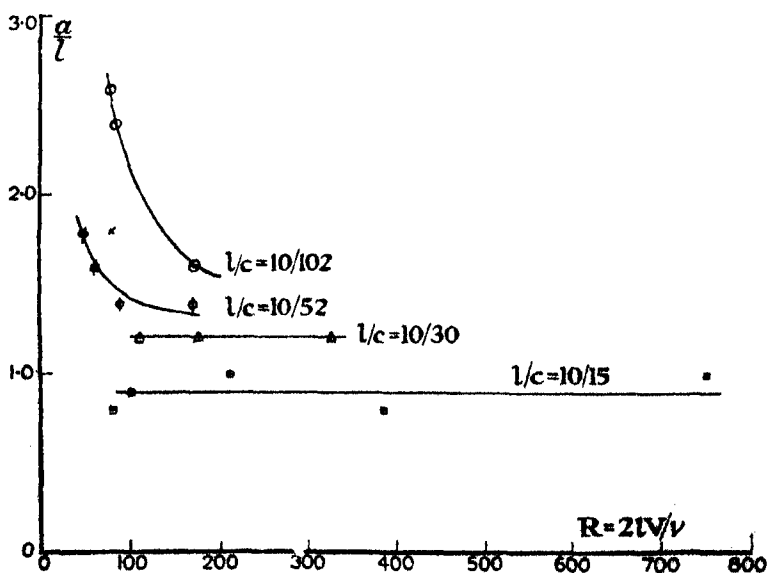


FIG. 10.—The ordinate in this figure is the ratio of the distance between the rows to the diameter of the cylinder. The abscissa is the Reynolds number. The value l/c gives the ratio of the diameter of the cylinder to the width of the channel. For further explanation, see paragraphs 2 and 6.

7. The Spacing Ratio.

The variation of the spacing ratio a/b with R and l/c is given by fig. 11. It appears that, within the limits of experimental error, the spacing ratio in the regular part of the trail of vortices is 0.32, and that this value holds for all systems in which the distance between the rows is less than one-third

* 'Proc. Roy. Soc.,' A, vol. 116, p. 170 (1927). See in particular p. 191.

← — Direction of Flow.

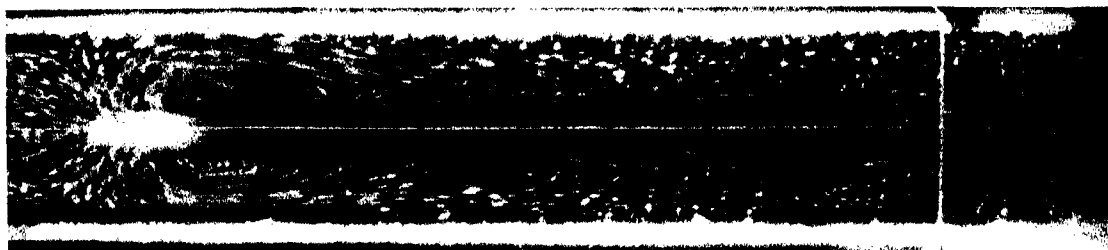


FIG. 1.—Ref. 13₁.

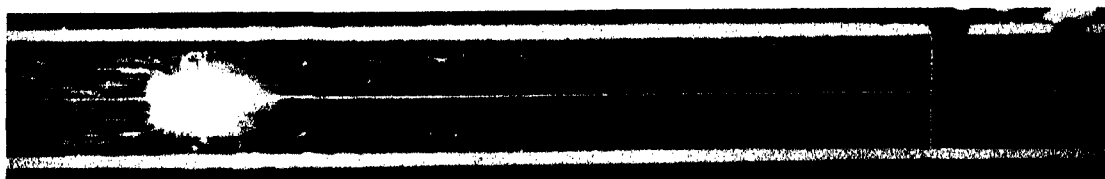


FIG. 2.—Ref. 43₂.



FIG. 3.—Ref. 36₁.

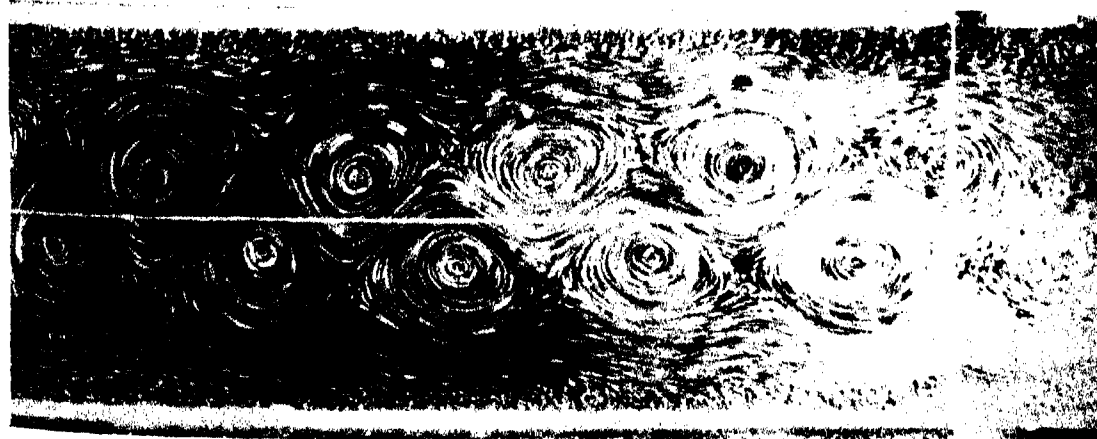


FIG. 4.—Ref. 34₃.

(Facing p. 128.)

← Direction of Flow.

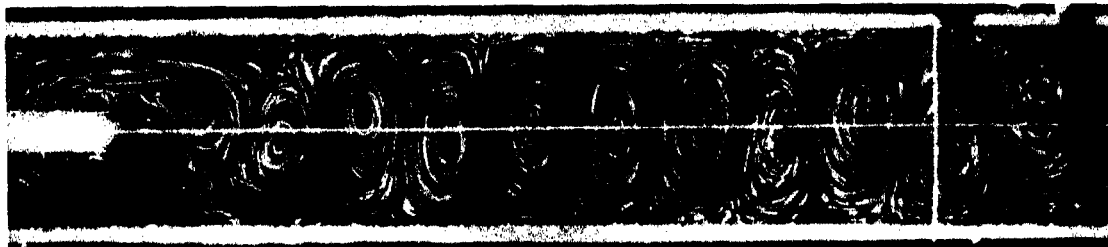


FIG. 5 — Ref. 37₁.

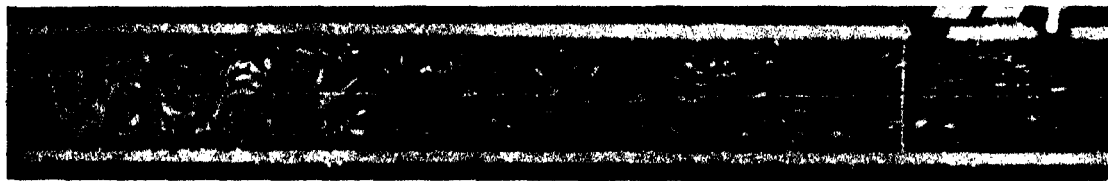


FIG. 6. Ref. 22₄.



FIG. 12.

(approximately) of the distance between the channel walls. This value may hold for even wider systems but there is a break between the values $l/c = 1/3$ and $l/c = 2/3$ in our investigations, and we are only justified in putting $1/3$ as the upper limit. There must, however, be a gradual increase in the value of a/b , for we find that when the obstacle is wide, say, l/c equals $2/3$, the mean spacing ratio is approximately 0.45 .

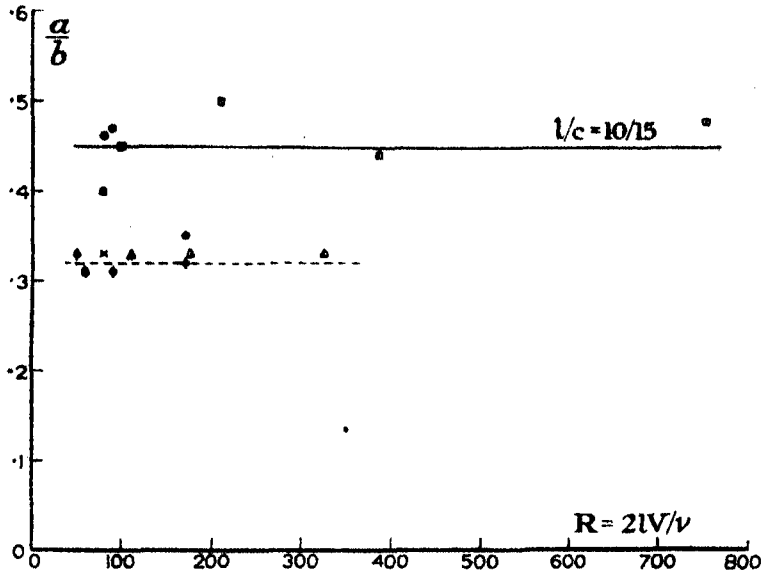


FIG. 11.—The ordinate in this figure is the spacing ratio of the vortex pattern in the regular part of the wake—that is the ratio of the distance between the rows to the distance between consecutive vortices on the same row. The abscissa is the Reynolds number. The unbroken line is meant to give the mean value of the spacing ratio for the case where the diameter of the cylinder is two-thirds of the distance between the channel walls. The broken line gives the mean value of the spacing ratio for the other cases considered. For further explanation, see paragraphs 2 and 7.

The above determinations agree with the experimental evidence of Fage and Johansen (*loc. cit.*) and with the results obtained by Bénard* in that the values of the spacing ratio are greater than those determined from Karman's theory. In particular, the results obtained by Bénard agree very well with those given here. For example, Karman says that the spacing ratio of those vortices near the obstacle should be approximately 0.36 , and that, as we recede from the cylinder, the ratio should diminish and attain its limiting value 0.28 . In

* 'C. R.' vol. 182, p. 1523 (1926).

criticising this from the experimental point of view, Bénard says that the sense of the variation is often reversed and quotes as examples four results taken at random from his films, the change being from 0.09 to 0.21, 0.15 to 0.26, 0.17 to 0.41, 0.38 to 0.49. In some cases the initial variation was in the sense indicated by Karman, but just as frequently the limiting value was attained almost immediately. Even then, the limiting value did not agree with that of Karman, the mean value being 0.32 (extremes 0.13 and 0.49). Variations in a/b did not appear to be connected with variations in R and l/c .

The failure of Bénard to note the increase in a/b with increasing l/c is probably due to the fact that the width of the obstacle was never very large in comparison with that of the channel, or to a larger range of error than is apparent here. The ultimate dissolution of the double row was probably assumed to be due to diffusion, and not instability, and so Bénard speaks of the attainment of a limiting value for a/b . This, however, is negated by Fage and Johansen. In particular, the agreement as to the mean value of the spacing ratio 0.32, between the investigations of Bénard and those recorded here should be noted. The variations from the mean are smaller here than in Bénard's account.

8. *Summary.*

The investigations deal with the vortex pattern in the wake behind a cylinder of circular cross section in channels of different breadths.

There is a limiting value of the Reynolds number below which no vortices are shed. There is an ill-defined upper limit of the Reynolds number above which it is impossible to speak of the formation of a double row of vortices. The bad definition of the upper limit is due to the rapid diffusion of vorticity, to the speed with which instability sets in and to the formation of a surface wave of appreciable amplitude over the free surface at high Reynolds numbers. Within these limits double rows of vortices of varying degrees of regularity are seen in the wake. The stream line patterns are very similar to those derived from the theoretical investigations. Immediately behind the obstacle there is a turbulent region and just beyond this a tendency to regularity manifests itself. Still further along the wake (in almost all cases) the vortices show a tendency to spread from the axis of the channel and this is interpreted as an indication of the ultimate dominance of the destabilising influences. The plotted paths of the vortices strongly support this view. The approximate constancy of the longitudinal spacing between consecutive vortices in every experiment was noticeable.

Curves are given showing the variation of the longitudinal spacing, lateral spacing, the spacing ratio, the velocity of the vortices, with increasing Reynolds numbers, for different values of the ratio of radius of cylinder to width of channel. The ratios of the dimensions of the street to the radius of the cylinder decrease with increasing Reynolds numbers, and attain asymptotic values. At a fixed Reynolds number the ratios of the dimensions of the street to the radius of the cylinder decrease as the width of the cylinder becomes greater in comparison with the width of the channel.

The spacing ratio of the vortex pattern in the regular part of the wake is 0.82 and this value holds for all systems in which the distance between the rows is less than one-third of the distance between the channel walls. There must, however, be a gradual increase in the spacing ratio, for when the diameter of the cylinder is two-thirds of the width of the channel, the ratio is 0.45.

The ratios of vortex velocity to cylinder velocity increase with the Reynolds number and attain asymptotic values. At a fixed Reynolds number the velocity ratio increases with the width of the cylinder.

APPENDIX, by M. SCHWABE.

These experiments were conducted in the Kaiser Wilhelm-Institut für Strömungsforschung, at Göttingen. A water tank of length 60 cm., breadth 20 cm., and depth 13 cm. was used in preference to a larger one of length 340 cm., and breadth 60 cm., because the water comes to rest more quickly in the smaller tank than in the larger one. However, in order to be able to use the fittings of the larger tank, the smaller tank was placed inside the larger one. The distance between the walls, $2c$, was altered by having movable walls fitting into holders so placed that their distances apart were 168, 102, 52 and 30 mm.

The obstacle was a circular cylinder of diameter 1 cm., but only when $2l/2c = 2/3$ did we use a cylinder of 2 cm. diameter. The obstacle was carried through the water by a carriage moving on the flanges of the big tank (see fig. 12, Plate 10).

The cylinder was mounted on a -formed holder, the vertical sections of which were very close to the walls, and whose horizontal section was very close to the bottom of the tank. By this arrangement the mount of the cylinder is not visible in a photograph of the wake. The carriage moved on two rails, only one of which was used as a leading rail, so as to avoid the difficulties that may arise when the rails are not exactly parallel. It was driven by an

electric motor ; a closed cable was laced over a roller drawn by the motor with which the carriage was coupled by means of a simple clip.

The well-known method of strewing the free surface with aluminium powder was used in order to show the stream line motion. Care was taken not to diminish the mobility of the free surface by strewing too thickly with aluminium powder.

The photographic apparatus was an old roll film apparatus that was rebuilt some time ago, as described in 'Naturwissenschaften,' p. 1050 (1925), for the purpose of taking similar photographs. Briefly it can be said that by inserting a "Maltese cross," the ratio of exposure time to transport time was increased to about 10 : 1, whereby it was made possible to have each picture follow on the preceding one without a great interval of time elapsing between them. Two arc lamps were used for lighting. The lamps were attached to movable arms on a column standing on a second car which could be coupled with the carriage that carries the cylinder. This, however, is not relevant to the main purpose of the investigation, so that it is unnecessary to go more deeply into the details of construction. The film apparatus was put between the two lamps ; it rested over the tank, so that on the pictures the cylinder is seen not as a circle, but as a blurred strip, since it passes across the field of vision.

The figures necessary for the calculations were determined by a recording arrangement, already explained by H. Rubach, "Über die Entstehung und Fortbewegung des Wirbelpaares hinter zylindrischen Körpern," Dissertation, Göttingen, 1914. The velocity of the carriage was ascertained as follows : the positive pole of an accumulator was joined to the flat rail of the carriage carrying the obstacle. By the side of this rail contacts were arranged in two parallel rows on a wooden ledge, at distances of 3 and 1 cm. respectively. Wires connected these contacts to a chronograph and from there to the negative pole. During the motion the rail and contacts were touched by sliding springs. In order to record the beginning of a drive the arrangement was as follows : one spring (the same spring was used in every experiment) was placed just before the first contact so that a very small movement would cause the circuit to close, which in its turn would produce a small prick on the recording band and so mark the beginning of the drive. In addition, time was shown on the recording band by means of pricks at an interval of a second. The mean distance between these marks was 19.5 mm. Small deviations from this value are not to be regarded as faults of the apparatus, but simply as contact errors. Each picture was recorded by a prick.

In order to complete an experiment it was necessary to do as follows. The contacts for recording the velocity were prepared as described above. When the water had come to rest, the surface was strewn with powder and the chronometer was set going. All circuits to the chronograph were closed and the film apparatus was set in motion. The lamps were connected with the circuit and the recording band put in motion. Then the chronograph was connected with the circuit and at the beginning of an exposure the carriage and cylinder were set going. A short time after the cylinder had passed through the field of vision the experiment could be considered as finished.

On the pictures, the cross ledge of the carriage is seen at rest. The first picture of the motion is recognisable by the fact that this ledge is faintly seen. On the recording band this picture is to be recognised as the first of the records of velocity coming within the domain of the records of exposure time. It is therefore possible to record from this point the pictures both on the film and recording band, the distance gone by the cylinder, the time from the beginning of the motion, and the time between any two pictures. For the calculations, therefore, we need only take individual pictures, and the figures associated with them can be obtained quite easily from the recording band. Even when a few of the records were missing, as happened when the accumulator driving the chronograph gave out, and four of the records followed immediately upon each other, the missing values were obtained with sufficient accuracy by inter- or extrapolation. The pictures were enlarged to half natural size. In order to facilitate measurements on the pictures a taut wire parallel to the leading rail of the carriage was fixed over the tank. The wire passed over the centre of the cylinder and gave the position of the axis of the tank. Another wire was put across the tank at right angles to this so that the wires are seen on the pictures as co-ordinate axes to which measurements are to be referred.

As for the experiments, it can be said that at small velocities of about 0.5 cm. per second no street of vortices appears. This is already well known. At velocities of about 7 cm. per second the Karman street was very regular. At greater velocities, particularly in channels of small breadth, the street of vortices became so irregular and diffused so quickly that it is no longer possible to speak of a Karman street.

In general a pair of vortices in the unsymmetrical position, whose strength is much greater than that of the vortices of the street, remains behind the body. Then comes a region in which there are a few small irregular vortices. This is a turbulent region which is particularly strongly marked at great velocities

of the cylinder. This turbulent region, in which there is sometimes a three-dimensional motion, eventually gives place to a region in which the vortices of the Karman street are formed periodically. Often, however, and especially at small velocities, when the formation of vortices is very regular and stable, the Karman street is seen from the beginning of the motion without any turbulent region. It should be noted also that the car and the body must be in motion for some time before they attain the final velocity. It is, therefore, necessary to let the body travel some distance until the final regular state has been developed, and disturbances need not be feared.

The velocity of the vortices moving in the wake of the body was determined as follows: The film negative was projected on to a table, and a paper marked out in millimetres was so placed on the table that the axes of the paper coincided with the axes of the projected film. The same position was therefore guaranteed for each film. The positions of the centres of the vortices from film to film were then marked on the paper. The distances between the marks were measured and the velocities were deduced by the use of the records. Naturally these measurements have no pretensions to absolute accuracy, for in some places the velocities are very small—0.05 cm. per second—and the percentage error rather big. It is at least possible, however, to see the order of the magnitudes of velocity.

It can be seen that the paths of the vortices, determined as described above, differ considerably. They can be divided into four groups. Experiments 2, 10, 41, 36 belong to the first group. The velocity of the vortices is very small; the vortices do not move very far from the point at which they were formed. The paths of the second group are more distinct—experiments 3, 4, 15, 34, 41. The vortices first move in a direction opposite to that of the cylinder and also towards the axis of the channel. They then spread from the axis and commence to follow the cylinder. The velocity of the vortices is from 8 to 12 per cent. of the velocity of the body. In the range of regression the velocity has an unimportant minimum. Experiments 16, 20, 21 are examples of the third group. The retrograde motion of the vortices has been lost, but the initial motion towards the axis, the withdrawal from the axis, and the motion following the cylinder are clearly visible. The velocity of the vortices is about 20 per cent. of that of the cylinder, and the motion is clearly influenced by the increasing value of l/c . This influence is seen more clearly in the fourth group to which experiments 22, 26, 28, 42, 44 belong. The vortices follow the cylinder immediately with a velocity that in some cases is greater than 50 per cent. of that of the cylinder.

It is easy to discover that the paths of the vortices under exactly similar conditions may be quite varied, as can be seen from a comparison of experiments 10 and 34 or 37 and 15. On the other hand, however, 14 and 36 (group 1) and 4 and 41 (group 2) show good agreement. The causes of these differences have not yet been investigated experimentally.

The Effect of Wind Tunnel Interference on the Characteristics of an Aerofoil.

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1. *Introduction.*

The effect of the walls of the enclosure on the measured values of the lift and drag experienced by an aerofoil is quite appreciable and it has been known for a considerable time that corrections must be applied to wind tunnel results before they can be applied to free air conditions. Prandtl* investigated the effect on an aerofoil in a free jet or circular tube both in the case where there is a uniform lift distribution, and in the case where there is an elliptic distribution of circulation. The elliptic distribution is of importance because it gives the minimum drag for a given lift. Glauert† by means of an approximate method found the induced drag and lift in a rectangular channel when there is a uniform distribution of lift. Terazawa‡ modified Glauert's method and obtained the exact solution for an aerofoil with uniform distribution of circulation in a rectangular channel. It is the object of this note to extend these results and to obtain the induced drag and lift in a rectangular channel when there is an elliptic distribution of lift. In addition, the discussion of Prandtl is briefly gone through because Prandtl's results are usually given as the first few terms of an infinite series, and it has not been noticed that the result can be obtained exactly. Glauert's work on the effect of plane barriers is briefly re-examined because, in his analysis, approximate expressions were summed

* "Tragflügeltheorie," II, 'Gött. Nach.,' p. 107 (1919).

† "Aerofoil and Airscrew Theory," p. 189 (1930), or 'R. and M.,' p. 867 (1923).

‡ 'Rep. Aer. Res. Inst. Tokyo Imp. Univ.,' vol. 4, p. 69 (1928).

over an infinite series of points, and at first glance it appeared that this would introduce some error of the same order as the result. In this note the summation is carried out rigorously and the approximations are introduced later, and it is seen that Glauert's expressions are first approximations to the actual values. The small divergences from Glauert's results obtained by Terazawa in two numerical cases are, in effect, the result of a slightly more accurate approximation.

From the practical point of view the results of this paper add little to what is known already, for the major corrections are given by the results of the approximate methods, but this note should fill in some small gaps in the theory of wind tunnel interference.

2. List of Symbols.

$2s, c, S$ = span, chord, area ($= 2sc$) of the aerofoil.

α, V = angle of incidence, velocity of aerofoil.

A = aspect ratio ($= 2s/c$).

ρ = density of the medium.

L, D = lift, drag of the aerofoil.

k_L, k_D = lift coefficient, drag coefficient of the aerofoil ($L/\rho SV^2, D/\rho SV^2$).

R = radius of circular tunnel.

b, h = breadth, height of rectangular tunnel.

C = area of tunnel section.

κ = circulation.

$$\xi = ys/R^2.$$

$$\zeta = s^2/R^2.$$

$$\tau = i2h/b.$$

$$q = \exp(i\pi\tau) = \exp(-2\pi h/b).$$

$$P_r = \sum_{p=1}^{\infty} \frac{1}{p^{2r+2}}, \quad Q_r = \sum_{p=1}^{\infty} \frac{(-)^{p+1}}{p^{2r+2}}, \quad R_r = \sum_{p=1}^{\infty} \frac{4p^{2r+1}q^p}{1+q^p}.$$

3. The Aerofoil in Free Air.

As an aerofoil moves through the air, filaments of vorticity are shed from the trailing edge and a thin wake of concentrated vorticity, which has been called a vortex ribbon, is formed. This sheet of vorticity is unstable and tends to roll up so that at some distance from the aerofoil the major portion of the vorticity is concentrated into two trailing vortices of equal strength but opposite sign, whose distance apart is slightly less than the span. As an

approximation therefore the wake may be considered as two trailing vortices springing from the tips of the aerofoil. There is also a circulation round the aerofoil, so that it may be considered as a line vortex of strength equal to the circulation, the strength of this vortex being equal to that of the two trailing vortices. This gives rise to the conception of the "horseshoe" vortex system as shown in fig. 1.

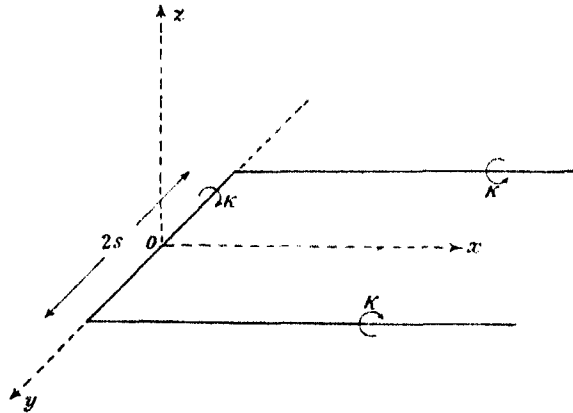


FIG. 1.

This is the simplest type of trailing vortex system and occurs when there is a constant circulation round the aerofoil. The lift L can be expressed in either of the forms

$$L = 2s\rho V\kappa = k_L S\rho V^2,$$

and the induced downward velocity at any point y on the aerofoil is

$$w = \frac{\kappa}{4\pi} \left[\frac{1}{s-y} + \frac{1}{s+y} \right] = \frac{\kappa}{2\pi} \frac{s}{s^2 - y^2} = \frac{k_L V}{\pi A} \frac{s^2}{s^2 - y^2},$$

or

$$\frac{w}{V} = \frac{k_L}{\pi A} \frac{s^2}{s^2 - y^2},$$

where A is the aspect ratio $= 2s/c$.

In general, however, the circulation is not constant along the span but is symmetrical about the centre, having its maximum at the centre and falling to zero at the tips. This is equivalent to a system of trailing vortices springing from each point of the trailing edge, the strength of the vortex starting from the point y being $-\frac{d\kappa}{dy} dy$. The distribution of circulation known as the

elliptic distribution is given by $\kappa = \kappa_0 \sqrt{1 - (y^2/s^2)}$, and in this case we get

$$\begin{aligned} L &= k_L S \rho V^2, \\ &= \int_0^s \rho V \kappa dy = \pi \kappa_0 \rho V s / 2. \end{aligned}$$

The induced downward velocity at a point y' on the aerofoil is given by the value, or rather the "principal value," of the integral

$$w = \int_0^s \frac{1}{4\pi} \frac{d\kappa}{dy} dy \left(\frac{1}{y - y'} + \frac{1}{y + y'} \right) = \frac{\kappa_0}{4s} = \frac{k_L V}{\pi A}$$

or

$$\frac{w}{V} = \frac{k_L}{\pi A},$$

so that the induced velocity is constant along the aerofoil. On account of this the drag is simply wL/V .

The net effect therefore of the trailing vortex system is to introduce a lift and drag. The walls of the enclosure also induce an effect so that measurements in wind tunnels differ from those obtained under free air conditions.

4. The Aerofoil in a Circular Tube or Jet.

In a tube the system of trailing vortices must be so compensated that the normal velocity at the walls is zero. This is done by introducing for every trailing vortex an image vortex of equal strength and opposite sign at a distance R^2/y , where R is the radius of the tube and y the distance of the vortex from the centre. In a jet the system must be so arranged that the pressure is constant over the surface of the jet. This is done by introducing image vortices as

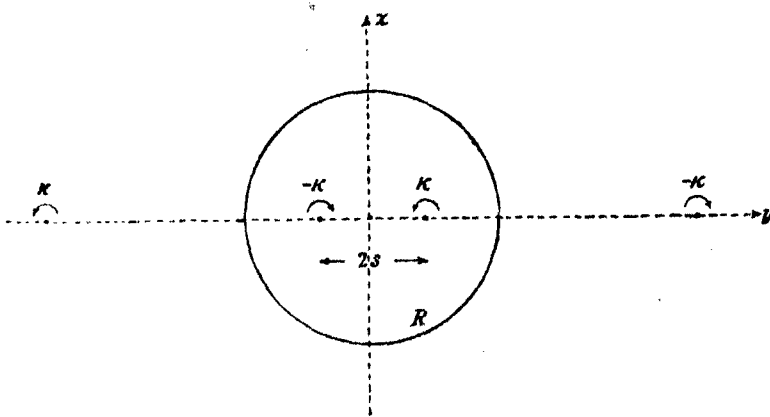


FIG. 2.

before, but with sign similar to that of the original trailing vortex. The results for the jet can therefore be easily deduced from that of the tube.

The induced upward velocity at a point y due to the walls is

$$\begin{aligned} w &= \frac{\kappa s}{4\pi R^2} \left(\frac{1}{1-\xi} + \frac{1}{1+\xi} \right) \\ &= \frac{1}{4} \frac{SV}{C} k_L \frac{1}{1-\xi^2} \\ &= \frac{1}{4} \frac{SV}{C} k_L (1 + \xi^2 + \xi^4 + \dots), \end{aligned}$$

where $\xi = ys/R^2$ and $C = \pi R^2$. This is equivalent to inclining the lift force forward by an angle w/V . The result of this is a reduction of the effective angle of attack by w/V , and a reduction of the drag D by $\int_{-s}^s \frac{w}{V} \frac{L}{2s} dy$. The drag coefficient $D/\rho SV^2$ is therefore diminished by an amount

$$\begin{aligned} \Delta k_D &= \frac{1}{\rho SV^2} \int_{-s}^s \frac{wL}{V \cdot 2s} dy = \frac{1}{4} \frac{S}{C} k_L^2 \frac{R^2}{2s^2} \log \frac{1 + (s^2/R^2)}{1 - (s^2/R^2)} \\ &= \frac{1}{4} \frac{S}{C} k_L^2 (1 + \frac{1}{3}\zeta^2 + \frac{1}{5}\zeta^4 + \frac{1}{7}\zeta^6 \dots), \end{aligned}$$

where $\zeta = s^2/R^2$. Hence in order to convert circular wind tunnel determinations to free air conditions, the corrections (which are to be added on) to the angle of incidence and drag coefficients are

$$\left. \begin{aligned} \Delta \alpha &= \frac{1}{4} \frac{S}{C} k_L (1 + \xi^2 + \xi^4 \dots) = \frac{1}{4} \frac{S}{C} k_L \frac{1}{1-\xi^2} \\ \Delta k_D &= \frac{1}{4} \frac{S}{C} k_L^2 (1 + \frac{1}{3}\zeta^2 + \frac{1}{5}\zeta^4 \dots) = \frac{1}{4} \frac{S}{C} k_L^2 \frac{1}{2\zeta} \log \frac{1+\zeta}{1-\zeta} \end{aligned} \right\} \quad (1)$$

In the case of a jet the corrections are the same as the above, but of opposite sign.

The assumption of elliptic distribution of lift modifies these results as follows. The circulation at any point y is given by the formula $\kappa = \kappa_0 \sqrt{1 - (y^2/s^2)}$. The induced upward velocity at y' due to the images of the trailing vortices at y and $-y$ is

$$\begin{aligned} dw_{y'} &= -\frac{d\kappa}{dy} dy \frac{y}{4\pi R^2} \left(\frac{1}{1-yy'/R^2} + \frac{1}{1+yy'/R^2} \right), \\ &= \frac{\kappa_0}{2\pi R^2 s^2} \frac{y^2 dy}{\sqrt{1 - (y^2/s^2)} [1 - (yy'/R^2)^2]}. \end{aligned} \quad (2)$$

The total lift can be expressed in either of the forms

$$\begin{aligned} L &= k_L \rho S V^2 \\ &= \rho V \int_{-s}^s \kappa dy = \pi \rho s V \kappa_0 / 2, \end{aligned} \quad (3)$$

so that the induced upward velocity at the point y' may be put in the form

$$w_{y'} = \frac{1}{\pi} \frac{SV}{C} k_L \int_0^1 \frac{\eta^2 d\eta}{(1 - \xi^2 \eta^2) \sqrt{1 - \eta^2}}. \quad (4)$$

The integral in this expression is equal to

$$\begin{aligned} &\frac{1}{\xi^2} \int_0^{\pi/2} \left(\frac{1}{1 - \xi^2 \sin^2 \theta} - 1 \right) d\theta \\ &= \frac{1}{\xi^2} \left[\int_0^\infty \frac{dt}{1 + (1 - \xi^2)t^2} - \frac{\pi}{2} \right] = \frac{\pi}{2\xi^2} \left[\frac{1}{(1 - \xi^2)^{1/2}} - 1 \right]. \end{aligned} \quad (5)$$

Hence

$$\begin{aligned} w_y &= \frac{1}{2} \frac{SV}{C} k_L \frac{1}{\xi^2} [(1 - \xi^2)^{-1/2} - 1] \\ &= \frac{1}{4} \frac{SV}{C} k_L [1 + \frac{3}{4}\xi^2 + \frac{5}{8}\xi^4 + \frac{35}{64}\xi^6 \dots]. \end{aligned} \quad (6)$$

The coefficient of ξ^6 is usually given as 35/128. This is a misprint that has remained uncorrected in reproductions of the expression, and the exact expression for the induced velocity given by equation (6) appears to have escaped notice. The corresponding decrease in the drag coefficient is

$$\begin{aligned} \Delta k_D &= \frac{1}{\rho S V^2} \int_{-s}^s \frac{w}{V} \cdot \frac{dL}{dy} \cdot dy = \frac{1}{\rho S V^2} \int_{-s}^s \frac{w}{V} \rho \kappa V dy \\ &= \frac{1}{4} \frac{S}{C} k_L^2 \left(1 + \frac{3}{4} \cdot \frac{1^2}{2^2} \xi^2 + \frac{5}{4^2} \frac{1^2 \cdot 3^2}{2^2 \cdot 3^2} \xi^4 + \frac{7}{4^3} \frac{1^2 \cdot 3^2 \cdot 5^2}{2^2 \cdot 3^2 \cdot 4^2} \xi^6 \dots \right) \\ &= \frac{1}{4} \frac{S}{C} k_L^2 (1 + \frac{3}{16} \xi^2 + \frac{5}{64} \xi^4 \dots). \end{aligned} \quad (7)$$

The expression for Δk_D can be expressed in terms of the complete elliptic integrals. The corrections with an elliptic distribution of circulation are therefore

$$\left. \begin{aligned} \Delta \alpha &= \frac{1}{4} \frac{S}{C} k_L [1 + \frac{3}{4}\xi^2 + \frac{5}{8}\xi^4 + \frac{35}{64}\xi^6 \dots] \\ \Delta k_D &= \frac{1}{4} \frac{S}{C} k_L^2 [1 + \frac{3}{16}\xi^2 + \frac{5}{64}\xi^4 + \frac{17}{1664}\xi^6 \dots] \end{aligned} \right\}. \quad (8)$$

These expressions should be compared with those obtained on the assumption of uniform lift, as given in equation (1).

5. *The Aerofoil between a Pair of Parallel Planes.*

This section is mainly preliminary to the case of the aerofoil in a rectangular channel and we shall only consider the case of uniform lift, the span of the aerofoil being assumed horizontal.

We shall first consider the effect of the vertical boundaries which are equidistant from the aerofoil and are a distance b apart. At the points $y = s$ and $-s$ there are two vortices of semi-infinite length and of strengths $+\kappa$ and $-\kappa$ respectively. In order to satisfy the boundary conditions, images of strength $+\kappa$ and $-\kappa$ must be placed at the points $(mb + s)$ and $(mb - s)$ respectively, where m assumes all integral values from $-\infty$ to $+\infty$. The distribution of velocity along the span is given by $d\Phi/dy$ where

$$\Phi = \frac{\kappa}{4\pi} \log \frac{\sin \pi (y - s)/b}{\sin \pi (y + s)/b}. \quad (1)$$

This gives

$$w = -\frac{\kappa}{4b} [\cot \pi (s - y)/b + \cot \pi (s + y)/b]. \quad (2)$$

The velocity induced by the walls is therefore

$$\begin{aligned} w &= -\frac{\kappa}{4b} [\cot \pi (s - y)/b + \cot \pi (y + s)/b - b/\pi (s - y) - b/\pi (s + y)] \\ &= \frac{\kappa}{2b} \left[\phi_0 + \frac{1}{2!} \frac{y^2}{b^2} \phi_2 + \frac{1}{4!} \frac{y^4}{b^4} \phi_4 \dots \right] \end{aligned} \quad (3)$$

where

$$\begin{aligned} \phi_{2n} &= b^{2n} \frac{d^{2n}}{ds^{2n}} \left(\frac{b}{\pi s} - \cot \frac{\pi s}{b} \right) \\ &= \frac{2}{\pi} \sum_{r=0}^{\infty} (2n + 2r + 1) (2n + 2r) \dots (2r + 2) P_{n+r} \left(\frac{s}{b} \right)^{2r+1}, \end{aligned} \quad (4)$$

and where

$$P_r = \sum_{p=1}^{\infty} 1/p^{2r+2}. \quad (5)$$

The induced velocity is not constant over the span and a first approximation is

$$w \approx \frac{\kappa}{2b} \phi_0 \approx \frac{\kappa}{2b} \frac{2}{\pi} \cdot P_0 \frac{s}{b} = \frac{\kappa \pi s}{6b^2} = \frac{\pi}{12} \frac{SV}{b^2} k_L, \quad (6)$$

which is the result obtained by Glauert. This is an upward velocity and tends to reduce the angle of incidence and drag coefficient as compared with unbounded conditions.

Similarly when the boundaries are horizontal and each at a distance $h/2$ from the aerofoil, the distribution of velocity along the span is given by $d\Psi/dy$ where

$$\Psi = \frac{\kappa}{4\pi} \log \frac{\tanh \pi (y-s)/2h}{\tanh \pi (y+s)/2h}. \quad (7)$$

This gives

$$w = \frac{\kappa}{4h} [\operatorname{cosech} \pi (y-s)/h - \operatorname{cosech} \pi (y+s)/h]. \quad (8)$$

The velocity induced by the walls is therefore

$$\begin{aligned} w &= \frac{\kappa}{4h} [h/\pi (s-y) - \operatorname{cosech} \pi (s-y)/h + h/\pi (s+y) - \operatorname{cosech} \pi (s+y)/h] \\ &= \frac{\kappa}{2h} \left[\psi_0 + \frac{1}{2!} \frac{y^2}{h^2} \psi_2 + \frac{1}{4!} \frac{y^4}{h^4} \psi_4 \dots \right], \end{aligned} \quad (9)$$

where

$$\begin{aligned} \psi_{2n} &= h^{2n} \frac{d^{2n}}{ds^{2n}} \left[\frac{h}{\pi s} - \operatorname{cosech} \frac{\pi s}{h} \right] \\ &= \frac{2}{\pi} \sum_{r=0}^{\infty} (-)^{n+r} (2n+2r+1)(2n+2r) \dots (2r+2) Q_{n+r} \left(\frac{s}{h} \right)^{2r+1}, \end{aligned} \quad (10)$$

and where

$$Q_r = \sum_{p=1}^{\infty} (-)^{p+1} / p^{2r+2}. \quad (11)$$

The induced velocity is not constant over the span and as a first approximation we put

$$w \approx \frac{\kappa}{2h} \psi_0 \approx \frac{\kappa}{2h} \cdot \frac{2}{\pi} Q_0 \frac{s}{h} = \frac{\kappa \pi s}{12h^2} = \frac{\pi}{24} \frac{SV}{h^2} k_L, \quad (12)$$

which is the result obtained by Glauert. In both these cases the effect of the walls is to reduce the angle of incidence and the drag coefficient.

6. The Aerofoil in a Channel of Rectangular Section.

The boundaries of the channel are the lines $y = \pm b/2$, $z = \pm h/2$. We shall discuss the cases of uniform and elliptic distribution of circulation. In the case of uniform circulation there are two semi-infinite trailing vortices of strengths $+\kappa$ and $-\kappa$ at the points s and $-s$ respectively. In order to satisfy the boundary conditions image vortices of appropriate sign must be introduced. These can be conveniently grouped into four sets:—

- (1) A set of strength $+\kappa$ at the points $s + mb + i2nh$.
- (2) A set of strength $+\kappa$ at the points $-s + mb + i(2n-1)h$.

(3) A set of strength $-\kappa$ at the points $s + mb + i(2n - 1)h$.

(4) A set of strength $-\kappa$ at the points $-s + mb + i2nh$.

The velocity along the span of the aerofoil is given by dF/dy where

$$F = \frac{\kappa}{4\pi} \log \frac{\vartheta_1\left(\frac{y-s}{b}\right) \vartheta_4\left(\frac{y+s}{b}\right)}{\vartheta_4\left(\frac{y-s}{b}\right) \vartheta_1\left(\frac{y+s}{b}\right)}, \quad (1)$$

where the periods of the ϑ functions are 1 and τ ($\equiv i2h/b$), and where q ($\equiv \exp(i\pi\tau)$) = $\exp(-2\pi h/b)$. The induced velocity at a point y is therefore

$$\begin{aligned} \frac{\kappa}{4\pi b} & \left[\frac{\vartheta_1'\left(\frac{y-s}{b}\right)}{\vartheta_1\left(\frac{y-s}{b}\right)} - \frac{\vartheta_4'\left(\frac{y-s}{b}\right)}{\vartheta_4\left(\frac{y-s}{b}\right)} - \frac{b}{y-s} \right. \\ & \quad \left. - \frac{\vartheta_1'\left(\frac{y+s}{b}\right)}{\vartheta_1\left(\frac{y+s}{b}\right)} + \frac{\vartheta_4'\left(\frac{y+s}{b}\right)}{\vartheta_4\left(\frac{y+s}{b}\right)} + \frac{b}{y+s} \right] \\ & = \frac{\kappa}{2b} \left[f_0 + \frac{1}{2!} \frac{y^2}{b^2} f_2 + \frac{1}{4!} \frac{y^4}{b^4} f_4 \dots \right]. \end{aligned} \quad (2)$$

where

$$\begin{aligned} f_{2n} & = \frac{b^{2n}}{\pi} \frac{d^{2n}}{ds^{2n}} \left[-\frac{\vartheta_1'\left(\frac{s}{b}\right)}{\vartheta_1\left(\frac{s}{b}\right)} + \frac{\vartheta_4'\left(\frac{s}{b}\right)}{\vartheta_4\left(\frac{s}{b}\right)} + \frac{b}{s} \right] \\ & = b^{2n} \frac{d^{2n}}{ds^{2n}} \left[\frac{b}{\pi s} - \cot \frac{\pi s}{b} + \sum_{p=1}^{\infty} \frac{4q^p}{1+q^p} \sin \frac{2p\pi s}{b} \right] \\ & = \sum_{r=0}^{\infty} \frac{2}{\pi} (2n+2r+1)(2n+2r) \dots (2r+2) P_{n+r} \left(\frac{s}{b}\right)^{2r+1} \\ & \quad + (-)^{n+r} (2\pi)^{2r+1} R_{n+r} \frac{(s/b)^{2r+1}}{(2r+1)!}, \end{aligned} \quad (3)$$

where

$$R_{n+r} = \sum_{p=1}^{\infty} \frac{4p^{2n+2r+1}q^p}{1+q^p}. \quad (4)$$

We see, therefore, that

$$f_{2n} = \sum_{r=0}^{\infty} \left[\frac{2}{\pi} (2n+2r+1)! P_{n+r} + (-)^{n+r} (2\pi)^{2r+1} R_{n+r} \right] \frac{(s/b)^{2r+1}}{(2r+1)!}. \quad (5)$$

As a first approximation—going to the first power of s , we get

$$f_0 = 2 \left[\frac{2}{\pi} P_0 + 2\pi R_0 \right] \frac{s}{b} = \left[\frac{\pi}{3} + 8\pi \sum_{p=1}^{\infty} \frac{pq^p}{1+q^p} \right] \frac{s}{b}, \quad (6)$$

which is Glauert's result. The exact formula for the induced velocity is therefore

$$\frac{w}{V} = k_L \frac{S}{C} \frac{h}{4s} \left(f_0 + \frac{1}{2!} \frac{y^2}{b^2} f_2 + \frac{1}{4!} \frac{y^4}{b^4} f_4 \dots \right), \quad (7)$$

and the induced drag coefficient

$$\Delta k_D = k_L^2 \frac{S}{C} \frac{h}{4s} \left(f_0 + \frac{1}{3!} \left(\frac{s}{b} \right)^2 f_2 + \frac{1}{5!} \left(\frac{s}{b} \right)^4 f_4 \dots \right). \quad (8)$$

In the case of the elliptic distribution of lift we must put $-\frac{d\kappa}{dy} dy$ instead of κ , where $\kappa = \kappa_0 \sqrt{1 - (y^2/s^2)}$, and integrate along the semi-span. Hence the induced velocity at a point y' is

$$\begin{aligned} \int_0^s -\frac{d\kappa}{dy} dy \frac{1}{4\pi b} & \left[\frac{\vartheta_1' \left(\frac{y'-y}{b} \right)}{\vartheta_1 \left(\frac{y'-y}{b} \right)} - \frac{\vartheta_4' \left(\frac{y'-y}{b} \right)}{\vartheta_4 \left(\frac{y'-y}{b} \right)} - \frac{b}{y'-y} \right. \\ & \left. - \frac{\vartheta_1' \left(\frac{y'+y}{b} \right)}{\vartheta_1 \left(\frac{y'+y}{b} \right)} + \frac{\vartheta_4' \left(\frac{y'+y}{b} \right)}{\vartheta_4 \left(\frac{y'+y}{b} \right)} + \frac{b}{y'+y} \right] \\ & = \frac{1}{2\pi} \int_0^s -\frac{d\kappa}{dy} dy \left[g_0 + \frac{1}{2!} \left(\frac{y'}{b} \right)^2 g_2 + \frac{1}{4!} \left(\frac{y'}{b} \right)^4 g_4 \dots \right], \end{aligned} \quad (9)$$

where

$$\begin{aligned} g_{2n} &= \frac{b^{2n}}{\pi} \frac{d^{2n}}{dy^{2n}} \left[-\frac{\vartheta_1' \left(\frac{y}{b} \right)}{\vartheta_1 \left(\frac{y}{b} \right)} + \frac{\vartheta_4' \left(\frac{y}{b} \right)}{\vartheta_4 \left(\frac{y}{b} \right)} + \frac{b}{y} \right] \\ &= \sum_{r=0}^{\infty} \left[\frac{2}{\pi} (2n+2r+1)! P_{n+r} + (-)^{n+r} (2\pi)^{2n+2r+1} R_{n+r} \right] \frac{(y/b)^{2r+1}}{(2r+1)!}. \end{aligned} \quad (10)$$

The induced velocity at a point y' is therefore

$$w = k_L \frac{SV}{C} \frac{h}{4s} \left[l_0 + \frac{1}{2!} \left(\frac{y'}{b} \right)^2 l_2 + \frac{1}{4!} \left(\frac{y'}{b} \right)^4 l_4 \dots \right], \quad (11)$$

where

$$l_{2n} = \frac{4}{\pi} \int_0^{\pi/2} \sum_{r=0}^{\infty} \left[\frac{2}{\pi} (2n+2r+1)! P_{n+r} + (-)^{n+r} (2\pi)^{2n+2r+1} R_{n+r} \right] \\ \times \frac{\sin^{2r+2} \theta}{(2r+1)!} \left(\frac{s}{b} \right)^{2r+1} \\ = \sum_{r=0}^{\infty} \left[\frac{2}{\pi} (2n+2r+1)! P_{n+r} + (-)^{n+r} (2\pi)^{2n+2r+1} R_{n+r} \right] \\ \times \frac{1}{2^{2r}} \frac{1}{(r+1) r^2 (r-1)^2 \dots 1^2} \left(\frac{s}{b} \right)^{2r+1}, \quad (12)$$

and the induced drag-coefficient is

$$\Delta k_u = k_u^2 \frac{S}{C} \frac{h}{4s} \left(l_0 + \frac{1}{2 \cdot 2^2 (1!)^2} \left(\frac{s}{b} \right)^2 l_2 + \frac{1}{3 \cdot 2^4 \cdot (2!)^2} \left(\frac{s}{b} \right)^4 l_4 \dots \right. \\ \left. + \frac{1}{(n+1) 2^{2n} (n!)^2} \left(\frac{s}{b} \right)^{2n} l_{2n} \dots \right). \quad (13)$$

The above equations give the induced effects as infinite convergent series, but for practical purposes it is only necessary to go as far as the first power of s/b and this gives

$$\Delta \alpha = \frac{w}{V} = \delta \frac{S}{C} k_L, \quad \Delta k_v = \delta \frac{S}{C} k_L^2, \quad (14)$$

where

$$\delta \approx \frac{h}{4s} f_0 \approx \frac{h}{4s} l_0 \approx \frac{\pi h}{b} \left[\frac{1}{1^2} + 2 \sum_{p=1}^{\infty} \frac{p}{1 + \exp(2p\pi h/b)} \right]. \quad (15)$$

In both cases the effect of the channel walls is to reduce the drag and the angle of incidence by the given amounts, so that these corrections must be added to the results to give the free air values. The elliptic distribution of circulation differs from the uniform lift case by a second-order term so that we should expect the corrections in both these cases to be identical if we only go to the first order, which is all that is necessary in practice. This identity is shown by the results, and they agree with those obtained by Glauert by his approximate method. Numerical investigation would only introduce small refinements into the figures given by Glauert, and as these already give the greater portion of the correction, no improvement on Glauert's results will be attempted.

The Exchange of Energy between Gas Atoms and Solid Surfaces.

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Introduction.

If gas molecules with average energy corresponding to a given temperature strike the surface of a solid at a different temperature, the average energy of the gas molecules leaving the surface does not in general correspond to the temperature of the solid but depends also on their average energy before striking it. In order to exclude complications due to the transfer of rotational energy we shall consider only monatomic gases. Let the average translational energy of the molecules before striking the surface at temperature T_2 correspond to a temperature T_1 , and let the average translational energy of the molecules after leaving the surface correspond to a temperature T_2' (see fig. 1). Modifying

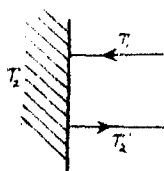


FIG. 1.

slightly a suggestion made by Maxwell* in a different connection, Smoluchowski† assumed that the change in the temperature of the gas molecules brought about by striking the surface is proportional to the difference between the temperature of the surface and that of the gas molecules before striking it; that is, that

$$T_2' - T_1 = a, \quad (T_2 - T_1). \quad (1)$$

The constant of proportionality a was later called the *accommodation coefficient* by Knudsen.‡ Smoluchowski applied this idea to explain the so-called temperature jump at the surface of a solid.

Knudsen showed that the simplest and most direct way to obtain values of accommodation coefficients is to work at low pressures so that the mean free path of the gas molecules is large compared with the relevant dimensions of the apparatus. For example, consider the heat loss from an electrically heated wire at temperature T_2 stretched down the centre of a tube at tempera-

* Maxwell, 'Phil. Trans.,' vol. 170, p. 231 (1879).

† Smoluchowski, 'Phil. Mag.,' vol. 46, p. 192 (1898); 'Ann. Physik,' vol. 35, p. 983 (1911).

‡ Knudsen, 'Ann. Physik,' vol. 34, p. 593 (1911); see also vol. 46, p. 641 (1915).

ture T_1 (see fig. 2). If the diameter of the wire is small compared with the free path λ of the gas molecules, the temperature drop between a and b is small compared with that between the wire and a , so that the molecules striking the wire can be assumed to be at the temperature T_1 of the tube b . a is a circle drawn at a distance λ equal to the mean free path of the gas molecules from the wire. Let the molecules leaving the wire have energy corresponding to a temperature T_2' . Applying the kinetic theory of gases to calculate the number of molecules striking unit area of the wire in unit time and, for a temperature change $(T_2' - T_1)$ the amount of energy they carry away, it was shown by Knudsen that Q the heat lost per unit area of the wire per second is for a monatomic gas and for small temperature differences given by

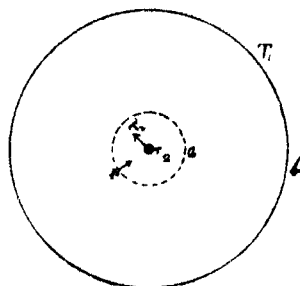


FIG. 2.

$$Q = 1.74 \times 10^{-4} \frac{p(T_2' - T_1)}{\sqrt{\mu T}} \text{ cal. cm.}^{-2} \text{ sec.}^{-1},$$

where p = pressure in dynes per square centimetre, μ = molecular weight ($O = 16$), and T = mean temperature.

Substituting in this equation from equation (1), we obtain

$$Q = 1.74 \times 10^{-4} \frac{pa(T_2 - T_1)}{\sqrt{\mu T}} \text{ cal. cm.}^{-2} \text{ sec.}^{-1}. \quad (2)$$

All the quantities in equation (2) except the accommodation coefficient a can be measured—the details will be considered later—and thus a can be determined. Knudsen and independently Soddy and Berry* proved that the heat loss Q was proportional to p and to $(T_2 - T_1)$ for a large number of gases. They also determined values of the accommodation coefficients.

Any attempt to develop a theory of the interaction between the gas and solid atoms necessarily involves a knowledge of the nature of the atoms which make up the solid surface. This means that the experimental data must be obtained from experiments carried out under such conditions that the surface of the solid is clean and free from films of adsorbed gas. The present experiments with helium and tungsten and nickel wires were carried out with this object in view.

* Soddy and Berry, 'Proc. Roy. Soc.,' vol. 83, p. 254 (1910); vol. 84, p. 576 (1911); see also Langmuir, 'J. Amer. Chem. Soc.,' vol. 37, p. 425 (1915).

Experimental Details.

If the surface of the wire from which the heat loss is measured is to remain free from adsorbed films for an appreciable time, it is essential that the helium be free from oxygen, nitrogen, and other adsorbable gases. Preliminary experiments showed that the necessary degree of purity could be obtained only if the helium were continuously circulated and passed through a charcoal tube immersed in liquid nitrogen before entering the experimental tube. To clean the wire it was heated to a high temperature and the observations to determine the accommodation coefficient were made as soon as it had cooled down. The arrangement of the apparatus is shown in fig. 3.

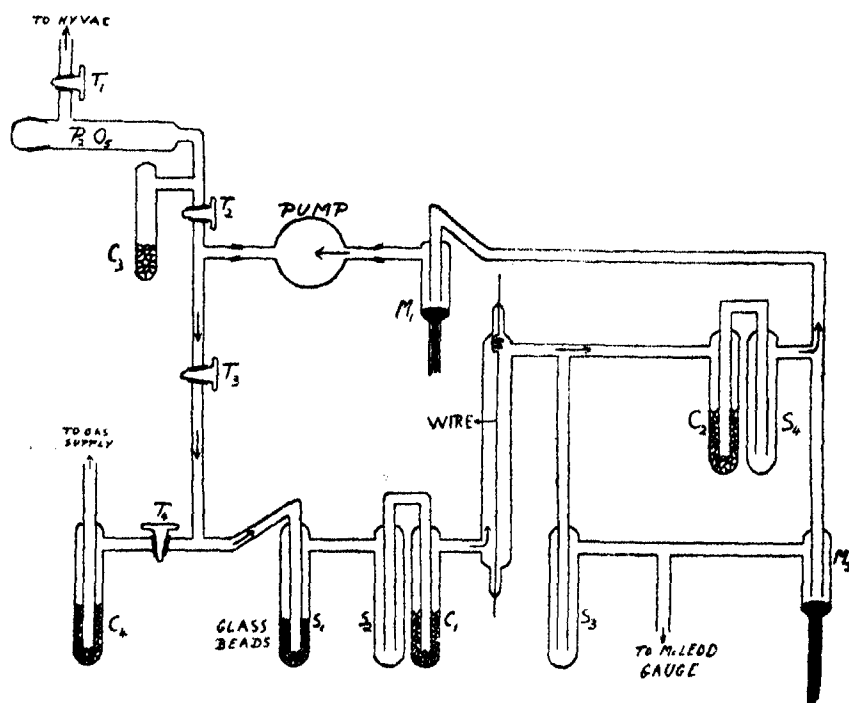


FIG. 3.

The tap T_3 was closed and the apparatus was evacuated and thoroughly baked out and degassed with the mercury cut-offs M_1 and M_2 both open. The cut-offs were then closed and the residual gas in the pump absorbed in the charcoal tube C_3 . While the apparatus and tubes between the trap S_1 and the charcoal tube C_2 were still hot, the traps S_1 , S_3 and S_4 and the charcoal

tube C_2 were immersed in liquid nitrogen so as to remove all mercury vapour. The tap T_2 was then closed and, by opening the tap T_3 and the cut-off M_1 , the apparatus was ready for circulating the gas, which had previously been purified by repeatedly passing it through a charcoal tube immersed in liquid nitrogen, and which after purification was stored in a reservoir and introduced in suitable quantities through the charcoal tube C_4 .

The charcoal tube C_1 , which purified the gas before it entered the apparatus containing the wire, was protected against mercury vapour carried by the stream of gas from the pump by the liquid air trap S_1 containing glass beads and by the trap S_2 . The charcoal tube C_2 prevented the diffusion into the apparatus of any mercury or other vapours from the pump that got through the trap protecting this charcoal tube. Diffusion of mercury vapour from the McLeod gauge and the cut-off M_2 was prevented by the trap S_3 . The charcoal tube C_2 provided sufficient resistance to the gas stream and no capillary was necessary.

The tube containing the wire was immersed in an electrically-heated thermostatically controlled oil bath, the temperature of which was measured with a mercury in glass thermometer which was compared with a thermometer standardised at the National Physical Laboratory. High precision in the thermometry was not necessary as temperature differences of 10 or 20° were used and an accuracy of 1 per cent. was ample.

The wire itself formed one arm of a Wheatstone Bridge. Reversal of the current in the bridge showed that to the order of accuracy required thermoelectric effects were negligible. The temperature excess of the wire was determined from its resistance as described below. Using Langmuir's tables for tungsten, the diameter of the wire was determined from the resistance after applying a small correction for the resistance of the molybdenum spring (see below) and the dumet leads. The result obtained was checked using a measuring apparatus kindly lent by Dr. Kapitza.

To determine the heat loss from the wire it was necessary to know the current passing through it. This was determined by measuring the whole current passing through the bridge with a direct reading Weston instrument which, using a potentiometer, was calibrated in terms of a standard resistance and a Weston standard cell. An almost negligible correction was made for the fraction of the total current passing through the ratio arms which were 1000 ohms each.

The procedure in carrying out a complete group of experiments was as follows.

Experiment I.

With the gas circulating, the tungsten wire about 0.007 cm. in diameter and 35 cm. long, which was held stretched by a spring of 0.03 cm. diameter molybdenum wire, was heated by a known current for 1 minute to a temperature well above 2000° C. to remove all adsorbed gas from its surface.* The zero of time was taken when this flashing current was switched off. The wire was reconnected to the bridge and a steady current sufficient to heat it 10° to 30° above its surroundings was passed through it. Resistance-time measurements were taken and it was checked that the pressure, current and bath temperature remained constant.

In order to determine the temperature excess of the wire above the bath from the resistance it was necessary to determine its resistance r_0 at the bath temperature. This was measured by reducing the current to a low value so that the excess temperature of the wire was small and again measuring the resistance. A small extrapolation to zero current gave r_0 . The temperature excess of the wire when the resistance was r_t was obtained from the expression $(r_t - r_0)/\alpha r_0$ where α , the temperature coefficient of the wire, was measured in a special experiment at another time by heating the whole bath up to various temperatures measured by the thermometer. This method of measuring the temperature excess avoided any possibility of the introduction of error due to a change in the constants of the wire being produced by the flashing.

Experiment II.

Immediately after experiment I and with the pressure and other conditions the same as in that experiment the wire was again flashed with the same current for 1 minute. The zero of time was again taken when the flashing current was switched off. The wire was reconnected to the bridge and a steady current sufficient to raise the temperature of the wire only about half a degree above its surroundings was passed through it. The sensitivity of the galvanometer in the bridge was increased by removing a series resistance so as to be approximately the same as in experiment I for a given change of resistance, and resistance-time measurements were again taken.

This experiment was just as sensitive as experiment I to residual temperature effects in the wire or gas due to the flashing of the wire, but, owing to the small temperature excess of the wire, it was very insensitive to show any time variations in the accommodation coefficient caused by the gradual formation of

* During this heating the wire was temporarily disconnected from the bridge by a system of mercury cup switches which could be worked rapidly.

adsorbed films after the cleaning. It therefore showed how long it took for the thermal disturbance due to the flashing of the wire to die out under the conditions of any particular experiment. The resistance fell rapidly to a definite value and then remained constant (see fig. 4).

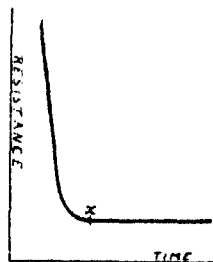


FIG. 4.

Experiment I on the other hand was sensitive to changes in the accommodation coefficient and after the time corresponding to the point *x* in fig. 4, which was usually about 4 minutes, showed a drift of resistance which continued for a long time.

Experiment III.

After experiment II was finished the tap T_3 (see fig. 3) was closed so that the circulation was stopped and the apparatus was evacuated to a pressure less than 10^{-5} mm. of mercury as measured on the McLeod gauge in order to determine the radiation and end loss.

Experiment IV.

After the completion of experiment III the gas was readmitted to the apparatus, which was then allowed to stand all night with liquid nitrogen on the traps. The next morning the gas was circulated and the accommodation coefficient was determined without any preliminary flashing of the wire. The radiation loss was also redetermined, but in no case had it ever changed appreciably from its value of the night before.

General Results.

Preliminary experiments showed that circulating the gas in itself made no difference to the value obtained for the accommodation coefficient; that is, that there was no appreciable drop of pressure between the apparatus and the McLeod gauge and that there was nothing analogous to convective cooling.

Other experiments showed that the pressure generally used (about 0.10 mm. of mercury) lay well within the region in which the heat loss was proportional to the pressure, that is, where the value of the accommodation coefficient was independent of the pressure. On one special set of three experiments carried out one after the other, in which the gas was circulated and the wire was flashed at the beginning of each experiment, the extrapolated accommodation

coefficients (see below) did not differ by more than 10 per cent., the pressures being 0.044, 0.10 and 0.14 mm. of mercury, and there was no trend with pressure.

From each of the resistance measurements in experiment I taken after the time corresponding to the point x in fig. 4 a value of the accommodation coefficient was deduced. The results so obtained showed:—

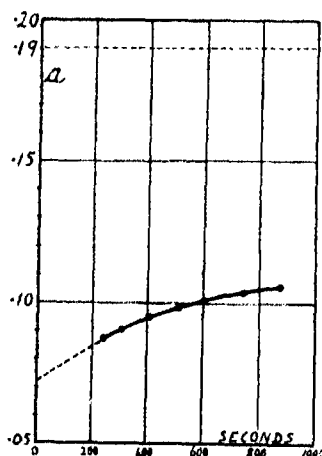


FIG. 5.

- (1) That the accommodation coefficient for a cleaned wire is considerably smaller than that for a wire which has stood overnight and is covered with films of adsorbed gas.
- (2) That the accommodation coefficient of a cleaned wire shows a definite drift with time, presumably owing to the gradual building up of adsorbed films by the residual impurities in the gas.

A typical example of the results obtained is shown in fig. 5. The points marked are measured values of the accommodation coefficient taken after the time ($3\frac{1}{4}$ minutes)

corresponding to the point x in fig. 4. A small extrapolation to zero time gives the accommodation coefficient for a clean surface. The accommodation coefficient 0.19 measured after the apparatus had stood all night as described is shown on the figure for comparison.

Numerical Values for a Smooth Surface.

To deal with the numerical results in detail it is necessary to consider the effect on the measured accommodation coefficient of the roughness of the surface. By comparing results obtained with polished platinum and with platinum black, Knudsen showed experimentally that with the same substance increasing the roughness of the surface increases the measured value of the accommodation coefficient. The cause of this effect is illustrated in fig. 6. A molecule after leaving one part of the surface has a chance of striking another part before it returns to the body of the gas,

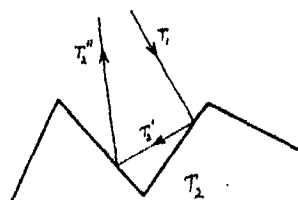


FIG. 6.

and on the average each molecule will make, say, n collisions with different parts of the surface before it returns to the body of the gas. If the molecules coming from the body of the gas have average energy corresponding to a temperature T_1 , and on the average after one collision corresponding to T_2' , and after two collisions to T_2'' , and so on, then, if T_2 is the temperature of the surface and a is the accommodation coefficient for a smooth surface,

$$\begin{aligned} T_2' - T_1 &= a (T_2 - T_1), \\ T_2'' - T_2' &= a (T_2 - T_2'), \\ &\dots\dots\dots \\ T_2^{(n)} - T_2^{(n-1)} &= a (T_2 - T_2^{(n-1)}). \end{aligned}$$

If now α_n is the effective or measured accommodation coefficient for a surface of such roughness that each molecule on the average strikes it in n different places before returning to the body of the gas, that is, if

$$T_2^{(n)} - T_1 = \alpha_n (T_2 - T_1),$$

it can be shown that

$$\left. \begin{aligned} \alpha_1 &= 1 - (1 - a), \\ \alpha_2 &= 1 - (1 - a)^2, \\ &\dots\dots\dots \\ \alpha_n &= 1 - (1 - a)^n \end{aligned} \right\} \quad (3)$$

Some values of effective accommodation coefficients for $n = 2, 3$ and 4 and for various true accommodation coefficients ($n = 1$) are given in Table I.

Table I.

$n = 1.$	$n = 2.$	$n = 3.$	$n = 4.$
$a.$	$1 - (1 - a)^2.$	$1 - (1 - a)^3.$	$1 - (1 - a)^4.$
0.05	0.10	0.14	0.19
0.06	0.12	0.17	0.22
0.07	0.13	0.20	0.25
0.08	0.15	0.22	0.28
0.10	0.19	0.27	0.36

It is known* that prolonged heating of tungsten to a high temperature produces microscopic irregularities in the surface. The first satisfactory results of the kind described in the foregoing section were obtained with a wire

* See Compton and Langmuir, 'Reviews of Modern Physics,' vol. 2, p. 157 (1930).

which, during a series of preliminary experiments and changes in the apparatus, had been subjected to many hours of degassing at a high temperature. This wire gave measured values for the accommodation coefficient of 0.12 clean and 0.40 after standing. After a further considerable period of heating the values were 0.18 clean and 0.55 after standing. A new wire was then used and was degassed by heating for about 1 hour to a temperature well above 2000° C. This wire gave 0.07 clean and 0.19 after standing (see fig. 5).

The observed changes in both clean and after standing values with prolonged heating of the tungsten are undoubtedly to be attributed to changes in the roughness of the surface. If we assume that the surface irregularities involved are in general large compared with the thickness of a few layers of adsorbed gas, the value of n (see equation (3)) will be the same for the clean surface and the surface which after standing has become covered with adsorbed layers. The procedure already described of measuring the corresponding values of the accommodation coefficient for a clean and a gas covered surface then enables us to correlate all the results given above and collected together in Table II. Let us assume that the lowest values 0.07 clean and 0.19 after

Table II.—Helium and Tungsten.

Measured accommodation coefficient.		Accommodation coefficient for smooth surface.	
Clean surface.	Dirty surface.	Clean surface.	Dirty surface.
0.07	0.19	0.07	0.19
0.12	0.40	0.05	0.19
0.18	0.55	0.05	0.19

standing refer to a smooth surface. Table I shows that, if the accommodation coefficient for a smooth surface is 0.19 and if the measured coefficient is 0.40, the roughness must be such that for seven-thirteenths of the molecules reaching the wire from the body of the gas $n = 2$, and $n = 3$ for the remaining six-thirteenths. Using these fractions it may be deduced from Table I that a measured value of 0.12 corresponds to a value of 0.05 for a smooth surface. Similarly for the third set of values, if the value for a smooth surface after standing is 0.19 and the measured value is 0.55, from Table I the roughness must be such that for one-fifth of the molecules reaching the wire from the body of the gas $n = 3$, and $n = 4$ for the remaining four-fifths. From these fractions it follows that a measured value of 0.18 for a clean surface corresponds to a value of 0.05 if the surface were smooth.

The values 0.07, 0.05 and 0.05 for a smooth clean surface are in satisfactory agreement. Since it is improbable that the measured values 0.07 clean and 0.19 after standing actually refer to an absolutely smooth surface, it is evident that the results given only fix an upper limit to the accommodation coefficient for a smooth clean surface, but it seems unlikely that the values given would differ from the true value by a factor greater than, say, two.

Similar measurements have been carried out with helium and a nickel wire.* The values obtained were 0.085 clean, and 0.20 after standing.

It is very probable that a nickel wire covered with several layers of adsorbed gas will have the same accommodation coefficient as a tungsten wire covered with adsorbed gas, and that the difference between 0.20 for nickel and 0.19 for tungsten is due to a slight difference in roughness. If we assume that this is the case, we obtain for the accommodation coefficient of helium on a smooth clean nickel surface the value 0.08.

This value is again an upper limit, but it is important to note that it refers to a surface of the same roughness as the tungsten surfaces for which the values 0.05 to 0.07 were obtained.

Discussion of Results.

The experiments of Stern† and his collaborators on the reflection and diffraction of molecular beams of hydrogen and helium from the surfaces of crystals of lithium fluoride, sodium chloride, etc., show, at any rate at angles of incidence up to 20° (glancing angle), that a large proportion of the atoms are diffracted or reflected, and although Stern has not observed all the diffracted beams, he has in some experiments accounted for 50 per cent. of the incident beam. This number shows that diffraction is not a phenomenon which occurs in only a small fraction of the encounters, but that it is of prime importance and that the whole question of the interactions between gas atoms and solid

* The nickel wire, which was 10.1 cm. long and about 0.006 cm. diameter, was not stretched by a spring but was arranged horizontally in a bulb 12 cm. in diameter. When it was flashed it just sagged under its own weight. For a short wire like this a correction, which can be calculated from the thermal conductivity and the electrical resistivity of the wire, is necessary and was applied for the fact that the end loss for a given mean excess of temperature is not exactly the same in the radiation loss experiment as in the experiment with gas present, i.e., it is a function of the surface loss. This correction did not amount to more than 10 per cent., so that the calculated value was sufficiently accurate. To clean the nickel wire it was heated to a temperature higher than 900°C . (cf. Germer, 'Z. Physik,' vol. 54, p. 414 (1929)).

† Knauer and Stern, 'Z. Physik,' vol. 53, p. 779 (1929); Estermann and Stern, 'Z. Physik,' vol. 61, p. 95 (1930).

surfaces must be treated from the point of view of quantum mechanics. Like an electron, an atom of mass m moving with velocity v must be considered as having de Broglie waves of wave-length

$$\lambda = h/mv \quad (4)$$

associated with it. Later in this paper it will be shown that the results of the present experiments do not appear to agree with the classical theory of the interaction at the surface, and this in itself suggests that some mechanism other than the classical must be postulated for the transfer of energy.

Atoms which are reflected or diffracted by the grating action of the atoms on the surface of the solid do not undergo any change of energy, so that, if all the atoms were diffracted or reflected, the accommodation coefficient would be zero. Thus the low values for accommodation coefficients observed in the present experiments are likely to be absolutely necessary if further experiments on atomic diffraction and reflection should appreciably increase the reflected and diffracted proportions already observed by Stern.

To obtain a complete quantitative explanation of the results we require to know from the point of view of quantum mechanics :—

- (a) What fraction of the incident atoms are reflected or diffracted.
- (b) What is the probable interchange of energy for those which are not reflected or diffracted.

The important point is that the present experiments show that the energy transfer to be accounted for by the theory is considerably less than would have been supposed from the earlier experiments in which the surfaces were covered with adsorbed films.

Maxwell's Theory.

In considering the motion of a gas past a solid boundary Maxwell* made the assumption that a fraction of the molecules incident on the surface are reflected without change of energy and that the remainder come into equilibrium with the surface before leaving it. The de Broglie waves and the regular arrangement of the atoms in the solid provide a mechanism whereby a fraction f of the incident molecules can be reflected or diffracted without change of energy. Since Maxwell's theory gives a definite picture and does, as we shall see, suggest an experiment, and since the energy transfer must be accomplished by those atoms which are not reflected or diffracted, we shall, while recognising the difficulties involved on the wave theory as they were on the classical, consider briefly the consequences of adapting the theory to the modern point of

* Maxwell, *loc. cit.*

view, and assuming that the fraction $(1 - f)$ of the incident molecules which are not reflected or diffracted come into equilibrium with the surface. The accommodation coefficient a is then, as Smoluchowski pointed out in discussing Maxwell's assumption, given by

$$a = 1 - f.$$

On this view the approximate agreement obtained in the present experiments between the accommodation coefficients of helium with clean tungsten (0.05 to 0.07) and clean nickel (0.08) surfaces of equal roughness simply means that approximately equal fractions (93 to 95 per cent. for tungsten and 92 per cent. for nickel) of the incident gas atoms are reflected or diffracted from the two surfaces. The fraction reflected or diffracted may be assumed to depend primarily on the regularity and perfection of the atomic grating. This grating is, of course, at least partially spoilt when it is covered with layers of adsorbed gas,* but for a clean surface, apart from the effect of intercrystalline layers between the microcrystals of the metal which owing to their small relative area is probably very small, the important factor disturbing the regularity of the grating is the temperature vibration of the solid atoms. At temperatures far removed from the melting point of the metal the amplitudes of these vibrations are small compared with the atomic spacing and for different metals do not in general differ greatly at a given temperature. We should, therefore, not expect large differences between the perfection of the atomic gratings of different metals† at the same temperature. The effect of varying the tempera-

* It is not possible to say whether the accommodation coefficient 0.19 for a gas covered surface is due to a persistence of regular structure in the adsorbed films even when several layers of gas are present.

† The order of magnitude of the ratio between the amplitudes of oscillation of nickel and tungsten atoms in the solids at the same temperature may be calculated as follows. If ν is the frequency of oscillation of a mass m , on which $K\xi$ is the restoring force for a displacement ξ from the equilibrium position,

$$1/\nu = 2\pi\sqrt{m/K} \quad \text{or} \quad K = 4\pi^2 m \nu^2.$$

If x is the amplitude of oscillation, the energy of the oscillation is $\frac{1}{2}Kx^2$. At ordinary temperatures, where the theorem of equipartition may be applied, this energy is the same for all substances at the same temperature. Let the suffix 1 stand for nickel and the suffix 2 for tungsten. We want the value of the ratio x_1/x_2 . We have $K_1x_1^2 = K_2x_2^2$ and, therefore,

$$x_1/x_2 = \sqrt{K_2/K_1} = (\nu_1/\nu_2) \sqrt{m_2/m_1}.$$

The atomic frequencies may be calculated with sufficient accuracy from Lindemann's melting point formula (see, for example, Roberts, 'Heat and Thermodynamics,' p. 432), and are $\nu_1 = 4.3 \times 10^{13}$ and $\nu_2 = 5.9 \times 10^{12}$. We have also $m_2/m_1 = 184/59$, and thus $x_1/x_2 = 1.3$. This may be taken as a direct measure of the relative imperfections of the atomic gratings of tungsten and nickel, since the atomic spacings only differ by about 10 per cent.

ture of the crystal on the intensity of diffracted beams is well known in the case of X-rays. A similar effect with atomic rays was observed by Estermann and Stern* who found an increase in the reflectivity when the temperature of the crystal was lowered, and Davisson and Germer† showed that with a beam of 343 volt electrons (de Broglie wave-length 0.66×10^{-8} cm.) the intensity of one of the diffracted beams in the Bragg diffraction pattern was increased about six times by cooling from 1000° C. to room temperature, while with a 54-volt beam (de Broglie wave-length 1.67×10^{-8} cm.) the intensity was only increased by a factor of about two. For comparison with the electron wave-lengths the following values for helium of the wave-lengths λ_m corresponding to the velocity of the maximum of the Maxwell distribution law are quoted from Stern's paper. Davisson and Germer's result suggests that the

Temperature.	λ_m .
$^{\circ}$ K.	cm.
100	0.974×10^{-8}
180	0.727
295	0.577
590	0.404

accommodation coefficient for a clean surface may be greater at lower temperatures than at ordinary temperatures owing both to the increase of the de Broglie wave-length of the gas atoms and to the diminution of the amplitude of the temperature oscillations of the atoms of the solid. Experiments are being arranged to test this point.

It may be mentioned that from the point of view of energy transfer the fact that the surface of the metal is composed of micro-crystals does not matter. So long as the mechanism is one of diffraction, it does not make any difference in what direction the atoms are diffracted. On the other hand in Stern's experiments any micro-crystalline structure or variation of crystalline orientation in the surface would diminish the intensity of the reflected and diffracted beams, and, therefore, we should expect that values of the fraction f deduced from diffraction experiments would be smaller than those deduced from experiments on accommodation coefficients.

* Estermann and Stern, *loc. cit.*, p. 115.

† Davisson and Germer, 'Phys. Rev.', vol. 30, p. 737 (1927).

Comparison of Results with Classical Collision Theory.

Baule* has suggested that the collisions between gas molecules and the atoms in a solid surface may be treated as collisions between elastic spheres. Using the laws of collision between such spheres, he has shown that, if the resultant velocity of a gas atom before collision is u_0 and that of the solid atom collided with is U_0 , and if u_1 is the mean velocity of the gas atoms after the collision averaged over all angles between u_0 and U_0 and all inclinations of the line joining the centres of the atoms at the moment of collision,

$$mu_1^2 = \beta mu_0^2 + (1 - \beta) MU_0^2,$$

where m = mass of gas atom, M = mass of solid atom, $\beta = (M^2 + m^2)/(M + m)^2$. Thus, if e_1 is the mean kinetic energy of gas atoms which have made one collision with solid atoms,

$$e_1 = \beta e_0 + (1 - \beta) E_0,$$

where e_0 = mean kinetic energy of the gas atoms before the collision : E_0 = mean kinetic energy of the solid atoms before the collision.

Thus

$$e_1 - e_0 = (1 - \beta) (E_0 - e_0), \tag{5}$$

and if all the atoms suffered only one collision with a solid atom, the accommodation coefficient a would be given by

$$a = (1 - \beta). \tag{6}$$

In the present experiments with helium on tungsten and helium on nickel the mass of the gas atoms is small compared with that of the solid atoms. In this case, unless the solid atom collided with happens at the moment of collision to have a velocity component *away from* the surface above a certain limiting value,† the gas atom is thrown back and, therefore, makes only one collision with an atom in this part of the surface.‡ By considering a two-dimensional case, it has been possible to obtain an estimate of the fraction of the solid atoms with a Maxwellian distribution of velocities, which have such velocities that a gas atom impinging on them with the mean velocity of the

* Baule, 'Ann. Physik,' vol. 44, p. 145 (1914).

† See Langmuir, 'Phys. Rev.,' vol. 8, p. 189 (1916), who dealt with head on collisions from this point of view.

‡ The effect considered here must not be confused with that dealt with earlier where we were considering the effect of roughness of the surface and the consequent possibility of a gas atom making a number of collisions in *different* places on the surface before returning to the body of the gas.

gas atoms is *not* thrown back and, therefore, makes two or more collisions in the same place.* For the cases which are important in the present experiments ($m/M = 0.0217$ for helium and tungsten, and $m/M = 0.0681$ for helium and nickel) the fractions involved are small, and for the two-dimensional case amount to less than 1 in 1000 for helium and tungsten and to 5 per cent. for helium and nickel.†

We shall write ν for the fraction of the gas atoms which make only one collision. The maximum possible effect on the accommodation coefficient of multiple collisions is obtained if we assume that the incident atoms which make more than one collision, *i.e.*, a fraction $(1 - \nu)$ of the whole, come into temperature (energy) equilibrium with the surface. That is, for a fraction ν of the incident atoms the accommodation coefficient is by equation (6) equal to $(1 - \beta)$, and for the remaining fraction $(1 - \nu)$ it is unity. Thus, with this assumption the actual accommodation coefficient is given by

$$a = (1 - \beta\nu). \quad (7)$$

Comparing equations (6) and (7) we see that the accommodation coefficient lies between the limits $(1 - \beta)$ and $(1 - \beta\nu)$. The values are tabulated in Table III together with the observed values, and the theoretical curve for $(1 - \beta)$ and observed values are plotted in fig. 7.

Table III.—Elastic Collision Theory.

Gas and solid.	$\frac{m}{M}$	ν	a (calculated) between limits.		a (observed).
			$(1 - \beta)$	$(1 - \beta\nu)$	
He and W	0.0217	1	0.042	0.043	0.05 to 0.07
He and Ni	0.0681	0.95	0.119	0.165	0.08

In making these calculations, the elastic forces between an atom in the surface of the solid and its neighbours have been neglected. It is to be expected

* In making the calculation it is necessary to make assumptions about the ratio of the radii of the gas and solid atoms and the ratio of the radius of the solid atoms to the distance between atoms in the lattice. These assumptions only affect the extent to which the solid atoms shield one another, *i.e.*, the angular limits between which collisions are possible and do not make any important difference to the order of the final result.

† Since the effect considered does not affect the subsequent argument, the detailed numerical calculations of these percentages will not be given here but will be published later.

that the effect of these elastic forces will be to introduce corrections to the theoretical curve given in fig. 7. It is reasonable to assume that the corrections will always be in the same direction, and for points near together on the curve will be of the same order. It will be seen, however, that the observed values do not fulfil the former criterion. If we assume that the observed values still need correction for roughness of the surfaces and we reduce them to one half, which seems the maximum reasonably allowable, we obtain the points shown and marked " $\frac{1}{2}$ value." Although these points fulfil the former criterion, they do not fulfil the latter. It may, therefore, be suggested that the observed values are inconsistent with the classical theory of collisions, as the considerations brought forward in the former section would lead us to expect. Further experiments with other gases will be carried out in order to attempt to test this point more definitely.

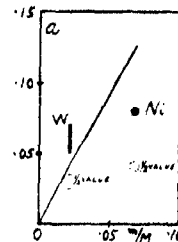


FIG. 7.

Summary.

Experiments on the accommodation coefficients of helium with tungsten and nickel surfaces have been carried out under conditions in which the surfaces could be freed from films of adsorbed gas and kept free long enough to obtain measurements for clean surfaces. The values obtained were 0.05 to 0.07 for tungsten and 0.08 for nickel, and are considerably lower than the values ordinarily obtained for gas covered surfaces (Soddy and Berry 0.3).

The results are discussed from the point of view of the reflection and diffraction of molecules and from that of the classical collision theory.

In conclusion it is a great pleasure to thank Sir Ernest Rutherford for allowing me to carry out these experiments in his laboratory and for his interest and advice during their progress. I wish also to thank Mr. R. H. Fowler for his interest and encouragement, and the Council of the Royal Society for a grant which enabled me to do the work.

The Mobility of Ions in Pure Gases.

By A. M. TYNDALL and C. F. POWELL, Bristol University.

(Communicated by A. P. Chattock, F.R.S.—Received June 11, 1930.)

Introduction.

Although determinations of the mobility of ions in gases have been made almost continuously during the last 30 years, the nature of the ions still remains obscure. The values obtained by different experimenters, using a variety of methods, differ by amounts far in excess of those to be attributed to observational errors and some methods yield results which are complicated and difficult to explain on any simple theory of the nature of the ion. The main facts which have emerged from the mass of experimental data are summarised in "Conduction of Electricity through Gases."*

It seems probable that in none of the experiments made hitherto has the gas under examination been spectroscopically pure. In many cases materials such as ebonite and sulphur have been in contact with the gas. In others the apparatus has been made gas-tight by means of waxed flanges or greased joints. In such conditions the purity of the gas leaves much to be desired. It is continually being contaminated by impurities such as water vapour and carbon dioxide coming from the walls of the vessel and from the metal parts of the apparatus as well as by the vapours from the wax, ebonite, etc. Such impurities may have large affinities for electrons and may unite with the positive ions to form groups. In such conditions, in a given gas, the ions may well consist of clusters of which the size and mass vary from one experiment to another. The reason why many observers have found the negative ions to be of molecular magnitude and not electrons in nitrogen, hydrogen, etc., becomes obvious, and it is not surprising that the actual mobilities found are smaller than those calculated theoretically from the standpoint of the classical dynamical theory of gases, assuming the ions to be monomolecular. The present writers, for example, found that in an experiment on nitrogen at a pressure of 600 mm., freshly introduced into an apparatus contained under a bell jar, the negative carriers consisted of a mixture of ions and electrons. The effect of the contamination coming from the walls was clearly shown by the fact that the number of "normal" ions increased, and of electrons decreased, on leaving the gas in the apparatus overnight.

* Thomson, Cambridge University Press, 3rd ed., 1928.

The effects of impurities are clearly of importance in the case of negative ions. In the case of the positive ions there are grounds for supposing that they may be even more critical. An electron, moving in an electric field through a gas attains a terminal energy which even at moderate fields (100 volts per centimetre) and high pressures (100 mm.), may be of the order of volts. If this energy is greater than the electron affinity of the molecules of the gas itself and any impurities in it, the electron, once it has attained its terminal speed will remain free even in the presence of large quantities of impurity. The positive ions on the other hand have a very small terminal energy and the monomolecular or atomic ions which are the primary products of the action of the ionising agent may be replaced, in the presence of extremely small concentrations of foreign molecules, by others of an entirely different nature. Either or all of the following processes may be involved.

(1) A cluster round the positive ion may form as the result of its impact with a foreign molecule possessing a marked dipole. At high gas pressures three-body collisions must be relatively common so that the probability of collisions leading to the union of the original ion with the impurity molecule may be high.

(2) Various recent results, obtained in experiments on the nature of the positive ions produced by electron impacts and examined by magnetic analysis, are satisfactorily explained on the view that a positive ion can capture an electron from any molecule or atom of lower ionisation potential with which it "collides." In particular in mixtures of argon and neon, Harnwell* concluded that transfers took place in accordance with the scheme



In a later paper† he obtained evidence in other mixtures for similar transfers; for example, from helium to hydrogen, neon to hydrogen, helium to nitrogen, and neon to nitrogen. Smyth and Stueckelberg quote‡ further cases. In more recent experiments, using a similar method but with a somewhat different procedure Kallmann and Rosen§ have obtained yet further evidence of the same phenomenon.

The results of all these workers are in accordance with the view now generally accepted, that the probability of an energy transfer is greater, the smaller

* 'Phys. Rev.', vol. 29, p. 683 (1927).

† 'Phys. Rev.', vol. 29, p. 830.

‡ 'Phys. Rev.', vol. 32, p. 779 (1928).

§ 'Z. Physik,' vol. 61, p. 61 (1930).

the energy to be transferred. The electron captured by the ion may enter either the ground state of the new atom, in which case the energy transfer is equal to the difference in the ionisation potentials of the old and new atoms, or it may enter a level of higher energy. In some cases the latter may be the more probable. We may regard the energy transfer as positive when the energy of the captured electron in the new atom is less than its original energy in the old atom, so that energy has to appear as a result of the interaction. Thus if a helium ion captures an electron into the ground state from a normal mercury atom, the energy transfer is equal to + 15 volts, since the ionisation

potential of mercury is 10 volts, and of helium 25 volts. In general, cases of both positive and negative energy transfer must be considered.

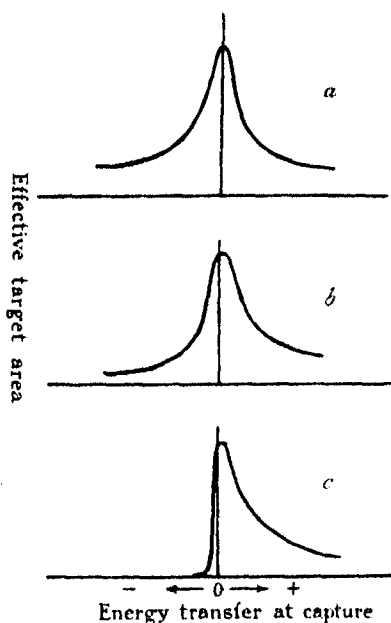


FIG. 1.

The actual probability of electron capture will depend upon the distance of closest approach of the reacting bodies, and upon the energy to be transferred at capture. Kallmann and Rosen discuss the problem qualitatively from the theoretical standpoint. They express their conclusions by drawing a curve showing the effective target area, presented by an atom to a high-speed positive ion, for those collisions which lead to the capture of an electron. Their curve is of the form shown in fig. 1, *a*. It will be seen that there is a maximum when the energy to be trans-

ferred from one atom to another at collision approaches zero, and that the curve is symmetrical about the ordinate through this maximum. That is, the probability of capture depends only on the magnitude of the energy transfer, and is independent of whether this energy has to be supplied from the kinetic energy of the ion, or is liberated and appears as an increase in the kinetic energy of the system after impact.

In the case of the impact of the high-speed positive ions with molecules as distinct from atoms, any energy liberated as the result of the interaction may appear either as kinetic energy or as vibrational energy in the new molecular ion. On the other hand, for collisions involving an absorption of energy the

required energy can only come from the kinetic energy of the high-speed ion because the vibrational energy of the molecule at ordinary temperatures is small. We may, therefore, expect that a transfer involving a given energy change will be more probable when energy has to be liberated than when it has to be absorbed. This introduces dissymmetry into the curve which may now take the form of fig. 1, *b*.

In the case of the capture of electrons by positive ions of very slow speed such as we find in gases at high pressures, the corresponding curve, whether for collisions with atoms or molecules, will be modified still further. There will still be a maximum for collisions involving zero energy change. But the curve must fall to zero at a point very close to this maximum as in fig. 1, *c*, since with these ions there is no kinetic energy available to satisfy the energy relations if capture involves an absorption of energy.

The following conclusion may be drawn from this curve. Consider, for example, positive helium ions moving through helium at a pressure of 300 mm. Assuming that the mean free path of the ions does not differ widely from the ordinary gas kinetic value, for which there is some evidence, they make, say, 2×10^9 molecular collisions per second. For an ion moving through molecules of its own gas the probability of transfer is a maximum. We may, therefore, expect the charge to remain associated with the same helium atom for only a few collisions. If the helium contains some impurity present to an extent of, say, one molecule in 10^5 it is probable that a considerable proportion of the charge originally carried by helium ions will arrive at the collecting electrode attached to molecules of the impurity. For once an impurity molecule has lost an electron, fig. 1, *c*, shows that it is very unlikely to be neutralised by recapture from a helium atom.

Evidently in the presence of minute quantities of even non-polar impurity, the values of mobility obtained may not be the true values for the gas under investigation.

(3) There is yet a third process which may lead to spurious results. In the process of ionisation metastable atoms are produced as well as ions, and under some conditions of excitation, their concentration may be high. Thus for neon in the positive column of glow discharges their number may be comparable with that of the positive ions. Now Franck and Jordan show that metastable helium atoms can react with atoms of impurity to give ions of the impurity by collisions of the second kind. This well-established phenomenon has been used by Penning* to explain the results of his experiments on

* 'Z. Physik,' vol. 46, p. 335 (1928).

the changes in sparking potential produced in neon by the addition of minute traces of mercury vapour or of argon.

It is, therefore, quite conceivable that in the presence of small quantities of impurity we may have two groups of ions starting off from the region of initial ionisation, one group consisting of the ions of the gas, and the other of ions of the impurity. The relative amounts of these will depend upon the relative numbers of ions and metastable atoms produced by the ionising agent and upon the concentration of impurity.

In the authors' opinion these processes are of paramount importance in determining the nature and hence the mobility of ions in gases. Their consideration emphasises the necessity for a high degree of purity of the gas especially in the investigation of positive ions in which the possible effect of small amounts of impurity has been largely ignored. In fact, one is led to the conclusion that no significance can be attached to the values of the mobility of the positive ion so far obtained in any gas.

To obtain definite results it is essential to adopt a design of apparatus in which the following conditions are satisfied: firstly, the method should enable one to separate with high resolving power mixtures of ions of different mobilities into their respective groups. None of the earlier methods in closed vessels permit of this, and methods involving a stream of gas do not allow of the use of pure gas. Secondly, the apparatus should be constructed entirely of glass and metal so that it can be subjected to a rigorous heat treatment in accordance with the requirements of modern vacuum technique. Only after this treatment should the purified gas be introduced.

A method described by the writers and Starr* and used in the experiments on nitrogen referred to above satisfied the first condition. The following paper contains a description of its modification to comply with the second condition and gives an account of the results obtained with two gases. It will be seen that the experiments on positive ions in helium in particular give striking illustration of the part played by minute traces of impurity.

Principle of the Method.

Briefly, the principle of the method employed is as follows:—

In fig. 2, *a*, A, B and C, D are 4 gauzes and E an electrode connected to an electrometer. Ions are brought up to the electrode A by a suitable directed

* 'Proc. Roy. Soc.,' vol. 121, p. 172 (1928).

field. The potential between A and B alternates with a certain frequency so that a flash of ions enters the main field B C once in every cycle. After crossing the space BC, in a time depending on the field and on their mobility, the ions reach the gauze C. The potential between C and D alternates in phase with

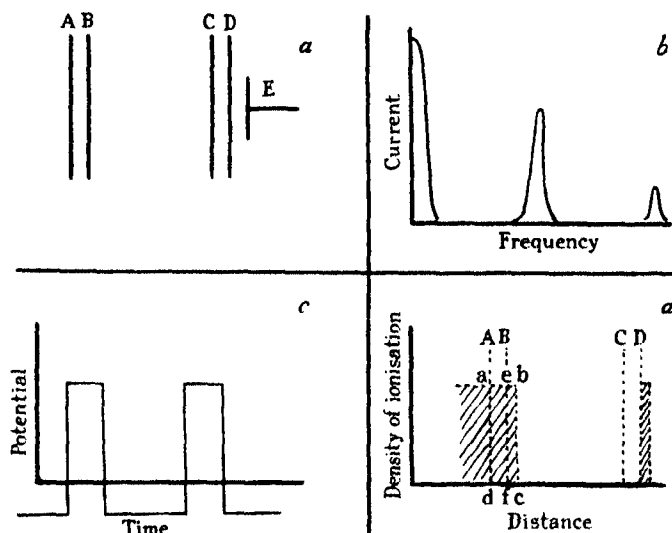


FIG. 2.

that between A and B so that for certain values of the frequency, ions of a given mobility arrive at C at the beginning of the advancing phase of the potential. Those of them which are not caught by the gauzes pass through to the collecting electrode E. If the current passing to the electrode E is plotted against the frequency of the alternating potential, and if ions of one mobility only are present, a curve similar to that shown in fig. 2, b, should be obtained.

Peak values of the current occur for those frequencies $\nu_1, \nu_2, \dots, \nu_n$, such that the time T, taken by the ions to pass from gauze B to gauze D is equal to $1/\nu_1, 1/\nu_2, \dots, 1/\nu_n$ where n is an integer.

When ions of different mobility are present, each class gives rise to its own characteristic series of peaks. The apparatus produces, in fact, an ionic spectrum, showing several orders.

In order to avoid confusion through overlapping, it is important to eliminate all but the first order spectrum. In addition it is essential to secure high resolving power for ions of different mobility. That both these conditions

can be fulfilled is seen from the following argument. Suppose for simplicity that the alternating pulse is of the form shown in fig. 2, *c*, and that no ions are absorbed by the gauzes. At the beginning of the voltage pulse, ions enter the space AB, and move across it. At the end of the pulse there will be a distribution of ionisation represented by the shaded area *abcd* in fig. 2, *d*. At the end of the pulse the field in the region between AB is reversed and the ions in it are caught by the gauze A. The ions represented by the area *ebcf* move across the main field. Let the frequency of the pulses and the mobility of the ions be such that the foremost ions reach gauze C at the beginning of the potential pulse which follows the one which admitted the ions to the main field. Then the entire flash of ions will have just passed through CD at the end of this potential pulse and will reach the electrode E. At higher or lower values of the frequency fewer ions will reach E.

By making the duration of the pulse short the width of the layer *ebcf* at the first order peak frequency can be made small compared with the distance AB. In this way the apparatus can be made to have high resolving power, the limit being determined by diffusion and the sensitivity of the electrometer. At the same time the second and higher order spectra will be suppressed because no ions will penetrate into the main field at the higher frequencies pertaining to them. Moreover, if this condition is fulfilled for one type of ion it holds generally for ions of any other mobility.

Similar conclusions can be drawn when the alternating pulse is of simple harmonic form, as in the present experiments. The necessary diminution of the width of the ionised layer can be secured by applying retarding voltages to the gauzes B and D so that ions enter A only during that portion of the cycle in which the voltage is in the neighbourhood of its maximum value.

There remains a possibility of overlap between the first order spectrum and a spectrum of zero order when one is dealing with ions of very different mobility. In practice this is found to occur only with a mixture of ions and electrons. Two examples are shown in the curves discussed later (figs. 5 and 6) in which a peak for the negative ions is superposed on the zero order curve of the electrons. If so desired this zero order spectrum can be cut out by using the alternating potentials out of phase by 180° .

In all the results which are discussed in this paper the values of the steady fields and the peak values of the alternating fields have always been maintained in the same ratio. Apart from diffusion effects, which have been found to be negligible, it will be seen that the current-frequency curve, due to the presence of a single group of ions, should be of a definite form whatever the pressure

and the absolute value of the fields. Any broadening in a peak must, therefore, indicate the existence of a distribution of mobilities in the group, or the presence of two groups of nearly equal mobility.

The Apparatus.

A diagram of the experimental tube is shown in fig. 3. The ionisation is produced by α -rays from polonium, the box containing the source being

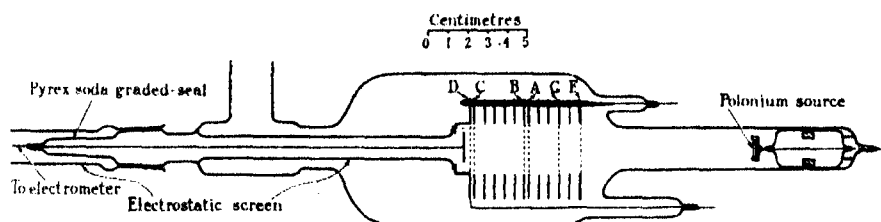


FIG. 3.

attached to a sliding glass tube surrounding an iron disc which enables the position of the polonium to be altered by means of a magnet. When the apparatus is being baked out (at 420°C.) the polonium is withdrawn into a glass tube projecting outside the furnace. After the main bake-out has been completed, the polonium is moved up and the projecting tube is in turn heated. To prevent the contamination of the apparatus by co-aggregate recoil of the polonium the source is covered with mica, the residual range of the particles being 5 mm. in air at N.T.P.

The gauzes were made by spot-welding thin nickel wires across circular holes in circular "staybright" steel plates. "Staybright" steel was chosen because it does not absorb mercury vapour. Besides the gauzes A, B, C, and D referred to above, two others G and F are included. In making an experiment the position of the polonium is adjusted so that no ions are produced beyond G. Ions produced between the source and F do not enter the measuring part of the apparatus, but those of one sign from the region FG are driven to A by a suitable field. The average age of the ions entering the main field can thus be controlled within certain limits.

The various fields are provided with guard rings to ensure uniformity and the method of insulation is the same as that used in the previous apparatus.*

* *Loc. cit.*

The leads to the various gauzes are taken out through three lead glass "pinches"; only one lead is shown in the figure. The main tube is of soda glass and the connection to the electrometer is taken out through a tungsten wire sealed into "pyrex," the soda glass and the "pyrex" being joined by means of a graded glass seal. Provided the gas is dry, "pyrex" is satisfactory as an insulator for this purpose, when serious surface leakage is prevented by means of earthed guard rings.

The earthed shielding tube for the electrometer lead is provided by a film of platinum on glass, this film being produced by painting the inner surface

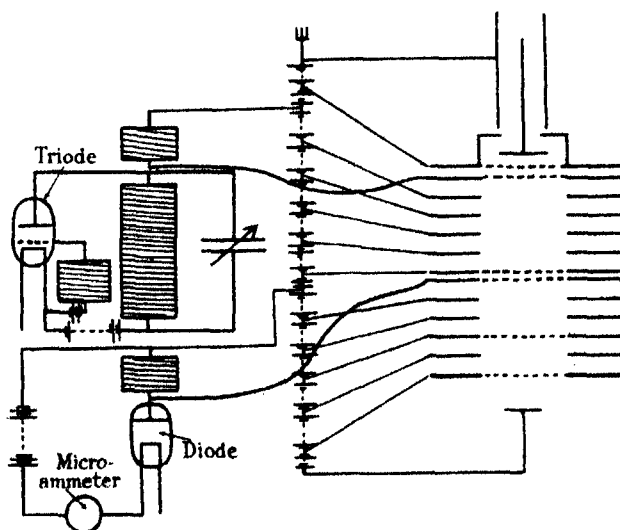


Fig. 4.

of a glass tube with "oil of platinum" and then heating the glass to the annealing temperature. The complete electrical connections are shown in fig. 4. The two alternating potentials required were obtained from a valve oscillator of which the frequency could be changed by altering the capacity of the condenser in the main oscillatory circuit. Two coils were mutually coupled with the main inductance of the oscillator. The peak values of the potentials induced in these two coils, measured by means of a diode voltmeter, could be adjusted by altering the coupling with the main inductance.

No iron was used in these inductances, and to obtain the frequency range from 50 to 6000 cycles per second three main oscillating coils with suitable coupled coils were built. In order to determine the frequencies given by the oscillator

for different values of the capacity of the variable condenser in the oscillatory circuit, the main oscillatory current was passed through a stretched piano wire passing between the poles of an electromagnet. Resonance vibrations were obtained by suitable adjustment of the length of the wire. With a given tension in the string the distance between two nodes is inversely proportional to the frequency. At the higher frequencies as many as 10 nodes and loops have been obtained. The wire was next adjusted to resonance with a standard tuning fork and the frequency corresponding to any condenser setting calculated for each of the three coils. It was shown by means of a four-plate cathode ray oscillograph that the fields across AB and CD were exactly in phase for all values of the frequency within the range supplied by the oscillator.

The currents to the electrode were measured by means of a Compton electrometer of high sensitivity to charge.

The distances between the gauzes were as follows : FG = 10 mm., GA = 15 mm., AB = 2 mm., BC = 25 mm., CD = 2 mm.

In a particular case the values of the potential between the plates were :—FG, 150 volts ; GA, 270 volts ; AB—22 volts ; BC, 450 volts ; CD—22 volts ; D-electrode, 60 volts. Peak value of alternating potential, 60 volts.

In other cases the fields were reduced in the same ratio and in the curves given only the value of the main field is quoted.

With the simple harmonic form of potential pulse the time taken by the ions in crossing the space between the gauzes C and D cannot be calculated accurately. This prevents the method from being used to make accurate measurements of the absolute values of mobility. One of us (C.F.P.) has designed an apparatus giving a square wave pulse of potential,* which should remove this objection in future experiments. The results given below show, however, that the method is entirely reliable for relative values. The values of mobility cited in the paper are calculated for atmospheric pressure on the assumption that the mobility of negative ions in dry air is 2.1.† No stress, however, is laid on these values as an error of, say, 10 per cent. will have no effect on the general conclusions of the paper.

Experiments with Air.

Before carrying out experiments in pure gases, determinations of the mobility of ions in dry air at various pressures were made. Langevin's law, namely, that the product of the mobility (k) and pressure (p) is a constant, has been

* In the press.

† Tyndall and Grindley, 'Proc. Roy. Soc.,' A, vol. 110, p. 341 (1926).

fully established by the work of previous investigators. We may, therefore, use this fact to test the reliability of the apparatus.

The results are shown in fig. 5 in which the electrometer current is plotted with the product of the frequency (ν) and the pressure. The product is

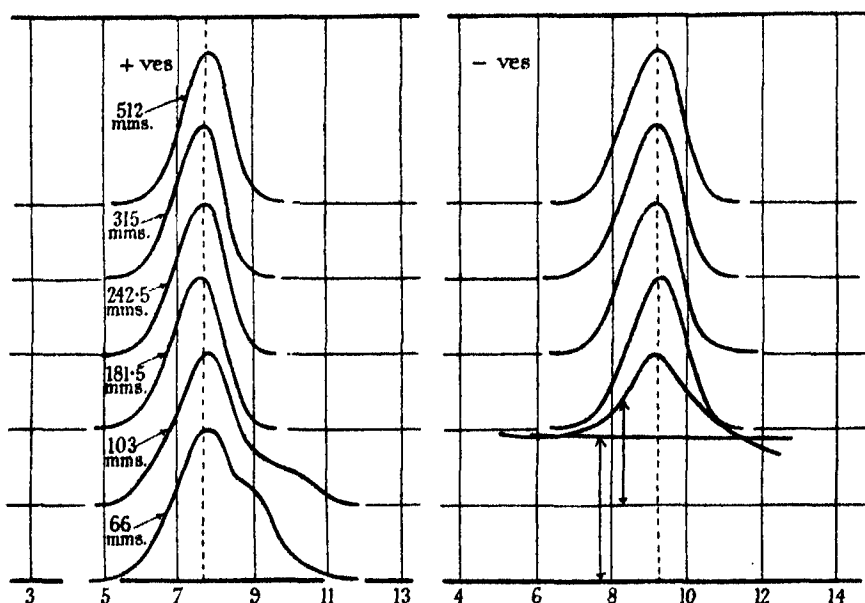


FIG. 5.—Air Frequency $\times$ Pressure (mm. $\times 10^{-4}$).
Main Field. 180 volts/cm.

proportional to kp . The scale of the electrometer current for each pressure is adjusted to make all the peaks of the same height and the curves are displaced vertically in order to exhibit the results in a convenient form.

Considering first the positive ions it will be seen that the maxima of the peaks all appear within experimental error at the same value of " νp ." It is exceedingly difficult to explain this result except on the assumptions (a) that Langevin's law holds, and (b) that the calibration of the oscillator is reliable.

Another possible source of error remains. It is conceivable, though highly improbable at the very low current densities employed, that serious contact potential differences may exist. Experiments were made, therefore, in which all the fields were reduced in the same ratio. It was then found that the peaks were exactly of the same form, their maxima occurring at frequencies directly proportional to the field values. It is evident from this that contact potentials play no disturbing part.

At the lowest pressure, 66 mm., there is an indication of a second group of ions of higher mobility which may be attributed to "initial" ions which Erikson originally found to exist in air under certain conditions of age. In dry air it is only at low pressures where the age is of the order of 0.001 second that one would expect "initial" ions to be present in measurable quantity. With negative ions, peaks obeying Langevin's law appear at all pressures except 66 mm. At this pressure there is at all frequencies an electrometer current approximately constant in value. This can only occur if the negative ions are electrons with a mobility which is so high that they shoot through the main field during the duration of a single pulse.

At 103 mm. the curve is the result of a superposition of a peak upon a uniform current. The peak occurs at the same value of " v_p " as for the other curves and the charge is evidently being carried by a mixture of electrons and "normal" ions. It is noticed also that the width of the "normal" ion peak is approximately the same as that at the higher pressures at which no electrons are present. This suggests that the electrons become attached to neutral molecules only in those regions where they have a relatively small velocity and not in the main field. At this pressure the value of E/p , where E is the electric force in volts per centimetre and p is in millimetres of mercury, was roughly 1.8 in the main field. Lattey* at pressure up to 29 mm. found electrons in air at much lower values of E/p provided traces of water vapour were excluded. In the present experiments the presence of water vapour does not appear to be critical, as electrons were found at 103 and 66 mm. whether the air was wet or dry.

At the higher pressures the continuous action of the α -rays may produce ozone and other products of chemical action in appreciable concentration, and it is not possible to attribute the formation of negative ions to any definite molecule.

Nitrogen.

The tests in air having proved to be satisfactory the apparatus was filled with purified nitrogen. Two sets of experiments were made. In the first of these the source of the gas was commercial nitrogen from a cylinder and in the second, heated sodium azide. Before generating the gas, the azide was heated for some hours *in vacuo*, at a slightly lower temperature than that necessary to produce decomposition, in order to remove water, carbon dioxide, etc. In both cases the gas was circulated several times over heated copper

* 'Proc. Roy. Soc.,' A, vol. 84, p. 173 (1910).

oxide and copper filings, and was then passed through liquid air traps into the "baked-out" measuring apparatus.

A selection of the results is shown in figs. 6, A, B and C. Considering first the negative ions, only one curve needs to be shown, namely, that in A (full line), because in every case investigated only electrons were found to be present. For purposes of comparison the type of curve given by the writers and Starr in an earlier communication, and referred to above, is inserted as a dotted line. This curve was obtained with nitrogen originally in a purified state but admitted

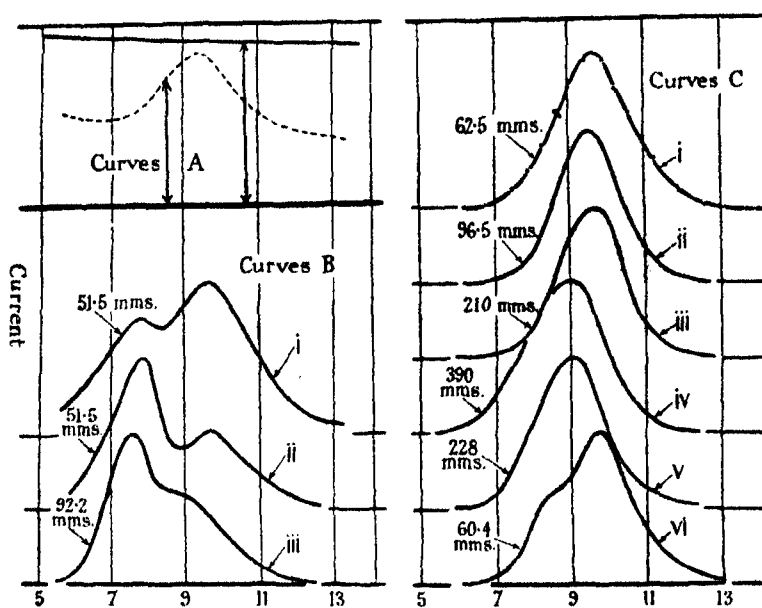


FIG. 6.—Nitrogen Frequency $\times$ Pressure (mm. $\times 10^{-4}$).
Main Field. 187 volts/cm.

to an apparatus sealed with wax and not subjected to heat treatment. Taken in conjunction with the present results it shows definitely that the existence of "normal" ions in nitrogen is an indication of the presence of contamination.

That the absence of any "normal" negative ions at these values of E/p is not a sufficient criterion of purity is, however, shown by the variability of the results obtained with positive ions. The results with cylinder nitrogen as the original source are given in curves B. These curves show two groups of ions varying in proportion even for two samples at the same pressure. Evidently the method of purification was not capable of removing traces of disturbing impurities contained in the cylinder nitrogen. It was for this reason that the

experiments with azide nitrogen were undertaken. The results are shown in curves C.

Curve C (i) at pressure 62.5 mm. was obtained as soon as possible after the gas had been admitted to the baked-out apparatus. The next curve C (ii) at pressure 96.5 mm. was obtained after more nitrogen had been added to the original sample, and similarly for the pressure 210 mm. It will be seen that in these curves only the one group of ions is present. It coincides in position with the group of higher mobility in curves B. Its position is also governed by Langevin's law.

The next addition of nitrogen bringing the pressure up to 390 mm. was not made until a week had elapsed. By this time traces of impurity not removed by the bake-out may well have accumulated in the gas, and there is evidence of this in the displacement of the curve C (iv) to a lower mobility. The subsequent curves at 228 mm. and 60.4 mm. were obtained by pumping off some of the gas. In the latter of these there is evidence of resolution of the peak into two groups and the curve is clearly tending towards the form of that shown in B (i).

The main conclusion to be drawn from these results is the great importance of minute traces of impurity on the mobility of positive ions in nitrogen. Indeed, it is quite possible that even the high mobility 2.1 deduced from C (i) for the sample of greatest probable purity is not the true mobility of a nitrogen positive ion moving through its own gas.

Helium.

The effects of minute traces of contamination are much more striking in the case of helium.

In the first experiments the gas was taken from a cylinder containing helium stated to be of 99 per cent. purity. It was first passed into a tube containing heated copper oxide, then successively into two degassed charcoal tubes immersed in liquid air, a second copper oxide tube and finally into two more charcoal tubes. A liquid air trap was interposed between the apparatus and the last tap. All taps were lubricated with apiezon L.* In a second series a tube into which sodium was electrolysed in the manner described by Taylor† was inserted after the second copper oxide tube. The purpose of this was to remove residual nitrogen.

* Burch, 'Proc. Roy. Soc.,' A, vol. 123, p. 271 (1929).

† Taylor, 'J. Sci. Instruments,' vol. 4, p. 78 (1927).

Some typical results for positive ions at a pressure of 359 mm. are shown in fig. 7. The scale of electrometer current is the same for all the curves but they are displaced vertically to exhibit the results in a convenient form.

Curve A, fig. 7, was obtained before the sodium discharge tube had been inserted in the purification plant and spectroscopic examination by electrodeless discharge showed the presence of nitrogen. The curve shows a main peak at mobility 14 and a hump suggesting a peak at a higher mobility of about 17, when reduced to atmospheric pressure. These mobilities are greatly in excess of those obtained for positive ions in helium by previous investigators.

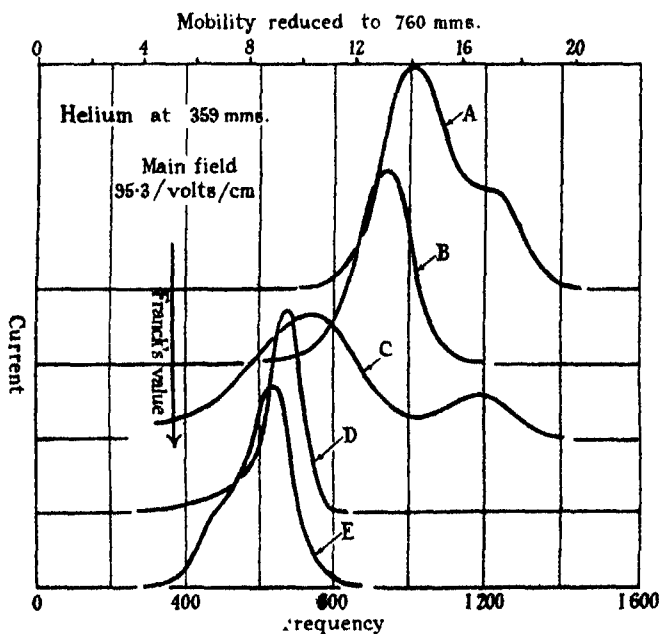


FIG. 7.

Thus Franck and Gelhloff ('Jahrb. Radioact.', vol. 9, S. 250) obtained the value 5.09 whether the gas was "pure" or slightly impure, and Rogers ('Phil. Mag.', ser. 7, vol. 5, p. 895, 1928) gives values ranging from 5.6 to 6.7.

The experiments were then repeated at a pressure of 300 mm. with precisely similar results and in agreement with Langevin's law as far as one could tell for two pressures not very widely different. The stopping power of helium is small and with the present apparatus 300 mm. was the lowest pressure at which it was possible to produce adequate ionisation in the localised region (i.e., the region GF, fig. 3).

To test whether the existence of two peaks was connected with the presence of nitrogen in the helium, the apparatus was baked out again and the gas repurified by the second method described. It was not tested by electrodeless discharge but a spark spectrum showed only helium lines. Though a spark spectrum is not so crucial a test for the presence of impurity as an electrodeless discharge, the gas was presumably purer in this case.

The results were somewhat unexpected because, although only one peak was obtained, it appeared at the somewhat lower mobility of 13. This mobility was shown to be independent of the field by the fact that the peak occurred at half the frequency when the fields were halved. An actual curve is shown in fig. 7, B.

Identical curves were obtained 1, 2 and 3 days later with the apparatus untouched. Ten days later, with liquid air maintained in the traps throughout the whole time, an entirely different curve C was obtained with two peaks, one at mobility 10 and another, a very small one, at one of the original high mobilities, 17.

It will be noticed that the main peak current is now smaller and the curve is spread out over a wide range of mobility. This suggests that the accumulation of impurity not detectable after 3 days had become appreciable in the subsequent week and that the ions were now a composite mixture of various mobilities. Even as it is, the mean mobility of the group is higher than that obtained by previous experimenters.

The next step taken was to remove the liquid air from the last trap so that any impurity which had been condensed in it, such as mercury or vapours from the tap grease vapour, could diffuse into the apparatus. The result is shown in D and it will be seen that the mobility of the ions is now well defined and is still smaller.

Finally, 1 per cent. of pure nitrogen from sodium azide was added to the helium. The result, seen in E, is a slight decrease of mobility which may be attributable to the change in the medium rather than to a change in the nature of the ions. There is a slight indication of the beginnings of a peak at a mobility in the neighbourhood of 7 cm. per second.

Throughout the sequence, experiments on the negative ions gave electrons and no indication of any "normal" ions.

The results for helium are, therefore, even more striking than those for nitrogen in demonstrating the effect of small amounts of impurity on the mobility of positive ions.

If the nature and amount of the traces of foreign gas present were known, it

might have been possible to explain these results in detail on the basis of the principles of electron capture, etc., discussed in the introduction to this paper. This is not possible at present because we have no adequate control of the minute traces of impurity involved, but we believe that it is in this principle that the explanation of the changes we have observed is to be found. That the results are particularly marked in helium is to be expected owing to the small size and mass of the helium ion. A marked decrease in mobility should occur when, by electron capture, the positive charge is transferred to some impurity molecule.

In the first sample of helium an attempt was made, at 300 mm., to apply the method of "clean up" by electrodeless discharge used successfully by Townsend and MacCallum* in their experiments at lower pressures on sparking potentials in helium and neon. The electrodeless discharge was produced by surrounding a side tube with the main oscillatory coil of a 5 kw. induction furnace. No appreciable change occurred in the mobility curve after $2\frac{1}{2}$ hours, though at these high pressures the discharge was weak. In the second series of experiments the discharge could not be applied owing to a breakdown in the furnace.

As in the case of nitrogen, we are, therefore, not yet in a position to give a value of the true mobility of helium positive ions in helium. But it is interesting to note that the mobility, 17, of the fastest ion we have observed is roughly three times that previously obtained, and is approaching the value 26.0 deduced by Hassé from the theory of Langevin for a monomolecular helium ion moving in its own gas. This lends support to the view that in the absence of all polar molecules a helium ion does not collect a cluster in its passage through a gas.

Before a value can be assigned to the true mobility of a helium positive ion moving through its own gas the experiments must be repeated under improved conditions. For this purpose it would be desirable to obtain the helium from another source, and, if possible, to redesign the apparatus so that lower pressures may be used. Under these conditions the helium should be neon free. At these lower pressures it should be possible to reduce considerably the chance of a helium ion colliding with an impurity molecule in its passage to the electrode.

The writers propose to continue the investigations on these lines, but the experiments will take time. Meanwhile, the results indicate the conditions necessary for obtaining significant values of the mobility of ions in gases, and

* 'Phil. Mag.,' vol. 5, p. 695 (1928).

may prevent others from wasting time on experiments in gases of doubtful purity.

Summary.

1. A method previously described by the writers and Starr for measuring the mobility of ions in gases has been modified to permit the measurements to be made in an all metal-glass apparatus which can be subjected to a rigorous heat treatment. The method has a high resolving power for ions of different mobility.

2. The apparatus was tested with dry air at various pressures and its reliability shown by the agreement of the results for positive ions with the well established law of Langevin. In dry air at 66 mm. and in a field of 180 volts per centimetre the negative carriers were all electrons. At higher pressures "normal" ions made their appearance.

3. Results in nitrogen emphasised for the first time the very great importance of small traces of impurity on the mobility of positive ions. In every case the negative ions were all electrons; but in spite of this the results with the positive ions were variable. Evidently the absence of "normal" negative ions is not an adequate criterion of purity.

4. The results in helium show even more strikingly the critical effect of traces of impurity on the positive ions. The maximum mobility recorded was of the order of 17. Slight contamination on standing was sufficient to transform the ions into a composite mixture of groups differing widely in mobility with a maximum at 10. After the removal of liquid air from a trap, inserted to prevent the access of mercury or vapours from the tap grease to the gas, the ions had a well-defined mobility of about 9.

5. This marked effect is to be expected from the principle of electron capture discussed by Kallmann and Rosen in a recent paper, according to which a positive ion on impact with a molecule of lower ionisation potential can capture an electron from the neutral molecule with a consequent change in the nature of the ion. At pressures of 100 mm. or more, to ensure that the measured mobility of the positive ion is the true mobility of an ion in its own gas, the residual impurity should be reduced to the order of a few parts in a million. In previous work on this subject nothing approaching this degree of purity has been obtained, and we are led to the conclusion that no significance can be attached to the values recorded in the literature of the mobility of the positive ion in any of the ordinary gases.

6. The highest value that we have so far obtained in helium for the mobility of the positive ion greatly exceeds those obtained by previous investigators;

it is of the same order as the value deduced from classical kinetic theory for the mobility of the positive monatomic helium ion moving through helium.

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The Absolute Intensities and Internal Conversion Coefficients of the γ -Rays of Radium B and Radium C.

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§ 1. *Introduction.*

It is well known that with many radioactive bodies the departure of the disintegration particle is followed by the emission of γ -rays. In addition to γ -rays of frequencies $\nu_1, \nu_2, \dots$, it is observed that there is an electronic emission consisting of several homogeneous groups whose energies can be written

$$\begin{array}{lll} h\nu_1 - K & h\nu_2 - K & \dots\dots\dots \\ h\nu_1 - L & h\nu_2 - L & \dots\dots\dots \\ h\nu_1 - M & h\nu_2 - M & \dots\dots\dots \\ \dots\dots\dots & \dots\dots\dots & \dots\dots\dots \end{array}$$

The energies of these groups are identical with those that would be produced by photoelectric absorption in the parent atom of the γ -rays emitted from the nucleus, and this phenomenon is frequently described as the internal conversion of γ -rays. By this is meant that in every case when the nucleus emits energy E this occurs in the form of radiation of frequency E/h , but that this does not always escape as such from the atom. In a fraction α of the cases the radiation is absorbed in the electronic structure and gives rise to a photoelectron, in the remaining fraction $(1 - \alpha)$ the γ -ray is emitted clear of the atom. The quantity α is termed the coefficient of internal conversion. Smekal* and

* 'Smekal, 'Z. Physik,' vol. 10, p. 275 (1922); Rosseland, *ibid.*, vol. 14, p. 173 (1923).

others have pointed out that there is no need and even no justification to consider the γ -ray ever to be emitted in the case of those atoms which give photoelectrons. All that can be truly inferred from the experimental facts is that the atom as a whole is capable of emitting energy E , and this it may do either in the form of a quantum of radiation $h\nu = E$, or in the form of an electron of energy $E - K$, or $E - L$, etc., followed by the appropriate excited K-, L-, X-radiations. The greater portion of this energy E is certainly resident in the nucleus, so that this second standpoint implies some type of what may be termed collision interaction between the nucleus and the electronic structure of the atom.

We have attempted to obtain some information on this interesting question by investigating the relative intensities of the γ -rays of radium B and radium C, and of the photoelectric groups associated with them.

Suppose we consider a large number of disintegrations of a certain radioactive body, and we find that monochromatic γ -rays of discrete frequencies $\nu_1, \nu_2, \dots$ are emitted. We will denote by p_r the probability that at any specified disintegration the energy $h\nu_r$ is emitted in one form or other, and further define as ${}_K\alpha_r, {}_L\alpha_r$, etc., the probability that this energy appears partly in the form of a photoelectron of energy $h\nu_r - K, h\nu_r - L$, etc.

Considering only the r th ray we see that from a large number N of disintegrations we shall obtain

$$N \cdot p_r \cdot {}_K\alpha_r \text{ electrons of energy } h\nu_r - K,$$

$$N \cdot p_r \cdot {}_L\alpha_r \text{ electrons of energy } h\nu_r - L,$$

and

$$Np_r [1 - ({}_K\alpha_r + {}_L\alpha_r + \dots)] \text{ quanta of radiation.}$$

If α_r is written for ${}_K\alpha_r + {}_L\alpha_r + \dots$ this becomes

$$Np_r (1 - \alpha_r).$$

The object of this paper is to describe measurements of the various quantities α , and on the basis of these results to discuss the question of the mode of energy interchange between the nucleus and electronic system. It will be seen that from these measurements we can also deduce the average number of quanta of each frequency emitted per disintegration, so that considered from another standpoint these experiments aim at finding the frequency of occurrence of the different processes which are associated with the γ -ray emission.

§ 2. *Method of Measurement.*

If a small thick walled platinum tube is filled with radon the γ -rays from the radium B and radium C formed from the radon will eject photoelectrons from the platinum. The resulting excited corpuscular spectrum can be recorded on a photographic plate by the usual method of semicircular focussing. The r th ray will give groups of which the most prominent will be that from the K level of energy $h\nu_r - K_{Pt}$. Suppose in addition a small amount of radium (B + C) is deposited on the outside of the platinum tube, then there will be a corresponding group from the radioactive material of slightly different energy $h\nu_r - K_{rad}$. Consider now the relative intensities of these two groups, one due to internal conversion in the radioactive atoms, the other to normal conversion in the platinum. The geometrical conditions are practically identical in the two cases, so that if during the exposure q and Q be the relative numbers of disintegrating atoms from the radium (B + C) on the surface of the tube, and from that formed from the radon inside the tube we can see that the relative intensities will depend mainly on the ratio

$$q \cdot p_r \cdot \kappa \alpha_r / Q p_r \cdot (1 - \alpha_r) \cdot \tau_K = q/Q \cdot \frac{\kappa \alpha_r}{1 - \alpha_r} \cdot \frac{1}{\tau_K},$$

where τ_K represents that part of the normal photoelectric absorption coefficient which corresponds to conversion in the K level. Experiments of this type should therefore lead to values of the quantity $\frac{\kappa \alpha_r}{1 - \alpha_r} \cdot \frac{1}{\tau_K}$. In practice it is

more convenient to carry out the experiment in two parts, photographing each type of spectrum in turn. The disadvantage of having to compare the intensities of lines on two different plates is outweighed by avoiding the excessive general background due to the superposition of that from each type of source. The experiments we are going to describe consisted essentially, therefore, in taking photographs of the natural β -ray spectrum of radium (B + C) and of the corresponding spectrum excited in platinum, under conditions when the geometrical conditions and exposures were known accurately, and then determining the relative intensities of corresponding groups by a photometric study of the plates. Although the method is simple in principle a great deal of time had to be spent in developing technique before reliable results could be obtained. The more important points are described in § 3.

We have stated that the relative intensity of the excited β -ray lines depends jointly on the intensity of the γ -ray, $p_r(1 - \alpha_r)$ and the absorption coefficient

of the K level of platinum τ_K . To establish this it is necessary to consider the factors influencing the form of the line. Fig. 1a shows the form of line given by a homogeneous group of electrons, such as a group in the natural β -ray spectrum. Fig. 1b shows the intensity distribution in an excited line. It is easy to see in a general way how the difference between 1a and 1b arises. While the electrons liberated in the platinum all have the same energy, the electrons that emerge from the tube will be heterogeneous. Those liberated

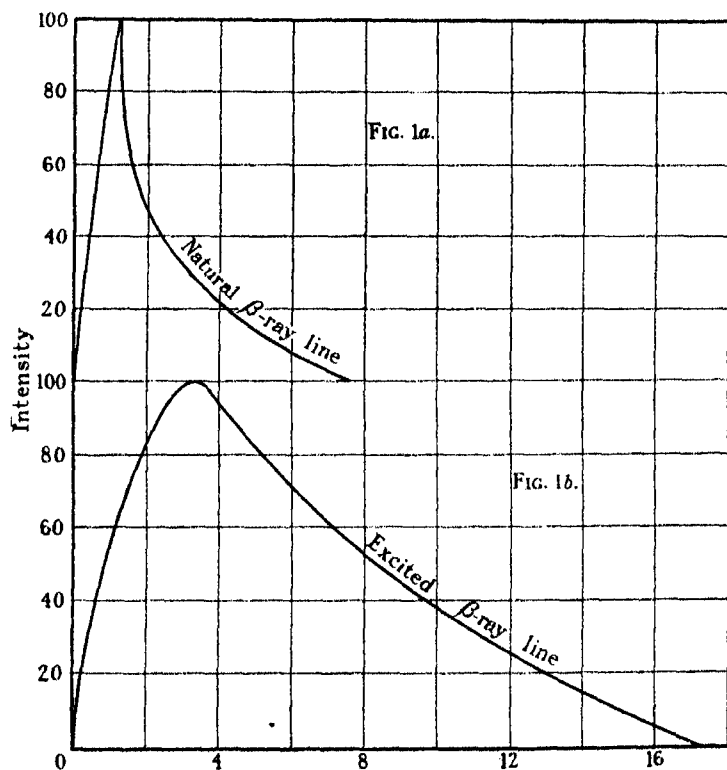


FIG. 1.

at the surface will have their full energy $h\nu, - K_{Pt}$, while those liberated beneath the surface will have lost various amounts of energy dependent on the distance traversed. Fig. 1b should, therefore, arise by adding together a series of curves like 1a but moved increasing amounts to the right. An attempt at a detailed theory is given in an Appendix. It depends on the experimental observation that to a first approximation all the excited lines had the same form 1b when brought to the same place on the photographic plate.

We have attempted to work out a detailed analysis of the shape of the excited β -ray line on this basis. This proved to be complicated and to involve close consideration of detailed points. We have, therefore, thought it best to give an account of this analysis at the end of the paper (Appendix I, § 6) and so to avoid breaking the main theme. The results that we obtain may be expressed as follows.

We denote by L_r the relative peak intensity of the natural β -ray line due to internal K conversion of the r^{th} γ -ray, and by G_r the peak intensity of the corresponding excited line. The justification for using this latter quantity is the experimental observation that to a first approximation all the excited lines had the same form *lb* when brought to the same place on the photographic plate. In both cases the peak intensity of the line associated with the strong γ -ray of energy 3.54×10^5 volts was put equal to 100.

We then find the following relation to hold

$$\frac{\kappa\alpha_r}{1 - \alpha_r} \cdot \frac{1}{\kappa\tau_r} = \frac{L_r}{G_r} \cdot \frac{H\rho \cdot \beta^3 f(\beta)}{B} \cdot S \cdot A.$$

"A" represents numerical factors, and quantities depending on the dimensions of the source and apparatus. The quantity $H\rho$ appears since the excited lines were always photographed at the same radius of curvature, so that in higher fields a given length of the plate received electrons over a greater range of velocity than in lower fields. S arises from consideration of the straggling of the electrons in emerging from the lower levels of the platinum tube, and $\beta^3 f(\beta)$ from the corresponding loss of velocity. The term $f(\beta)$ is an approximate correcting factor taken from Bohr's theory. The quantity B is determined experimentally from comparison of the intensities of corresponding natural and excited lines taken under known conditions of exposure. It will be seen in § 6 that this quantity B represents the essential point in our method of analysis. We found it to be independent of the frequency of the γ -ray due to the constancy of form of the excited lines.

We can also obtain from this formula the relation between the intensities of the γ -rays and the excited β -ray lines they give rise to by substituting $p_r \cdot \kappa\alpha_r$ cons. for L_r . It is then seen that the relative intensities of the emitted γ -rays, that is $p_r(1 - \alpha_r)$ are obtained by dividing the peak value of the excited line G_r by $H\rho \cdot \beta^3 \cdot f(\beta) \cdot \kappa\tau_r$. A small correction that was applied, but which is not given in the above formula is that for the absorption of the γ -rays in passing through the platinum to the outside layers from which the photoelectrons are ejected.

§ 3. *Experimental Procedure.*

It will be seen later from the analysis given in section 6 that to make use of the experiments on the excited spectrum it was necessary to have the source of radium B and radium C located in a known position inside a platinum tube. The method hitherto adopted in such experiments has been to fill a fine glass tube with radon and to place this inside a platinum sheath. This was not sufficiently definite for our purpose and had the additional disadvantage of unduly increasing the size of the platinum sheath. Instead we prepared a source in the following way. A platinum tube closed at one end was sealed to a normal apparatus for the supply and purification of radon. After purification the radon was condensed in the closed end of the platinum tube by application of a pad of cotton wool soaked in liquid air, and simultaneously the tube was cut off by a pair of pliers to the required length. The action of the pliers was to press the walls of the tube together making a joint sufficiently gas tight to contain the radon while the cut off end was soldered up. In this way it was possible to prepare tubes 1 cm. in length with an internal bore of 0.3 mm. and containing 100 to 150 millicuries of radon.

In order to stop most of the primary β particles from the radium B and radium C the walls of the tube were usually about 0.4 mm. thick.

The sources used to photograph the natural spectrum of radium B and C were prepared by exposing platinum wire to radon. At first the platinum wire had the same external dimensions as the platinum tube used in the other experiments, subsequently we found it an advantage for investigating the weaker lines to use wire 0.25 mm. in diameter and to determine by calculation the form and intensity of line that would be obtained from a source deposited on the thicker wire. We verified that the two methods gave the same results for the stronger lines.

The object of these experiments was to compare the intensities of the line obtained from the two types of source for equal numbers of disintegrating atoms. The calculation of the exposure was simple and definite in the case of the excited source since any slight unevenness in the deposit of radium B and C inside the tube would have scarcely no effect on the excited line. With the natural source, however, it was rare to find a uniform deposit on the wire, and it was not therefore possible to calculate the exposure, which was due to the radioactive material on one side of the source, merely from electroscope measurements of the total activity.* The active sources were therefore

* The unevenness of the deposit on an activated wire is well known and is due to minor factors in the preparation which would be more trouble to correct than the procedure adopted here.

fixed in the focussing apparatus to a holder which could be easily turned over and replaced exactly in the same position. Photographs were then taken in succession of the lines given by the radioactive material first on one half and then on the other half of the source. From these results the intensity that would have been obtained if the radioactive material had been uniformly distributed could at once be deduced.

The photographic method is usually somewhat difficult to apply to intensity measurements but we had to meet two difficulties that were peculiar to this experiment. In the first place the lines whose intensity we wished to measure were always superimposed on a continuous background. In the case of the natural photographs this was due simply to the continuous spectrum of the disintegration electrons, and in the excited photographs mainly to the recoil electrons liberated by the γ -rays from the platinum sheath. The photometer curves of the plates therefore showed certain increases of density at the positions of the lines, and owing to the gradient of the density-exposure curve of the plate becoming rapidly less at high densities, no increase in accuracy of the measurement of the density due to the lines could be obtained by increasing the exposure beyond a certain point. In the second place, as we have already explained, we found it necessary to compare the intensities of lines on different plates. Both these factors rendered it necessary to attempt the greatest possible accuracy that could be obtained, and we therefore spent a considerable time in investigating the most suitable application of the normal photographic methods to our particular problem. A metol developer was adopted after several others had been tried, and development was carried out for 8 minutes in a specially designed thermostat at 18° C. We found no advantage in continuing development beyond this point since the gain in density was counterbalanced by an increase in general development (chemical) fog. We attempted to ensure even development of different plates of the same development batch, by soaking the plates in distilled water before commencing development, and arresting the development by plunging the plates in a solution of sodium bisulphite. The fixing, washing, and drying of the plates was also carried out under standardised conditions, although there is no definite evidence that neglect of this would have introduced errors. Equality of treatment of the six to ten plates that constituted a development batch was ensured by fixing them in a holder in which they remained during the whole series of operations. The developer was continuously and vigorously stirred by moving a scraper to and fro about half a millimeter above the surface of the plates.

Special photographic plates were used which were very kindly prepared for us by the Research Department of Messrs. Ilford, Ltd. Standard X-ray emulsion was cast on large sheets of patent glass, and our plates were cut to the required size from the central portions of these large sheets. These plates proved very uniform in action, and greatly facilitated the work.

The "characteristic curve" of the plate, that is the relation between density and exposure was determined afresh for each development by exposing successive strips of a plate to a constant source of β -rays in a subsidiary apparatus.

The course of an experiment was therefore to take two or three plates of different lines from a natural source, and a similar number of plates of corresponding lines from an excited source. In each case the exposure was carefully noted. All these plates together with one or two calibration plates were then developed together.

The apparatus was the usual focussing apparatus using radii of curvature between 6.5 cm. and 9.0 cm. Great care was taken to satisfy the simple geometrical conditions required by the method, and especially to ensure that the geometrical conditions were the same for the natural and excited sources.

§ 4. *Experimental Results.*

Our measurements are set out in Table I. Column I shows the $h\nu$ of the γ -rays we were able to investigate, and columns II and III the relative peak intensities of the natural and excited groups, the intensity of the group due to the γ -ray 3.54×10^5 volts being in each case put equal to 100. In the notation of § 2 these two columns show the values of the quantities I_r and G_r . These figures represent the direct measurements of the density of the photographic plate corrected only for the density-exposure relation of the plate, the variation of photographic action with velocity of the particles,* and for small variations in the positions of the lines of the plates.† Owing to the homogeneity of the β particles forming the natural β -ray lines the figures in column II also show the relative values of the quantity $p_r \cdot \kappa \alpha_r$ as defined in § 2. The figures in column IV were obtained from those of column III by division by $H\rho \cdot \beta^3 \cdot f(\beta)$, where $f(\beta)$ has the meaning explained in the end of § 2. It will be seen from the account given there that column IV shows the relative intensities of the emitted γ -rays multiplied by the photoelectric absorption coefficient, that is the relative values of the quantity $p_r (1 - \alpha_r) \tau_\kappa$. The

* Ellis and Aston, 'Proc. Roy. Soc.,' A, vol. 119, p. 645 (1928).

† Wooster, 'Proc. Roy. Soc.,' A, vol. 114, p. 729 (1927).

Table I.

Col. I.	Col. II.	Col. III.	Col. IV.	Col. V.
$h\nu$ of γ -ray in volts $\times 10^{-6}$.	L_r relative peak intensity of the natural β -ray groups from K level, that is $p_r \cdot \kappa a_r$.	G_r relative peak intensity of the excited β -ray group from K level of platinum.	Relative values of $p_r(1 - a_r) \cdot \tau_K$.	$\frac{\kappa a_r}{1 - a_r} \cdot \frac{1}{\tau_K}$.
Radium B.				
2.43	80	34	67	0.040
2.97	91	66	89	0.035
3.54	100	100	100	0.034
Radium C.				
6.12	7.6	86	40	0.0065
7.73	0.60	6.7	2.4	0.0085
9.41	0.77	5.5	1.6	0.0164
11.30	2.42	13.5	3.4	0.0240
12.48	0.68	3.7	0.85	0.0270
13.90	0.17	3.3	0.70	0.0082
14.26	4.8	—	—	—
17.78	0.79	10.8	1.8	0.0150
22.19	0.18	2.5	0.35	0.0174

figures in column V are obtained from the ratio of the values in columns II and IV, and are expressed in absolute units by consideration of the geometrical factors of the platinum tube according to the detailed analysis given in § 6 in this table. The results given for radium B and radium C are directly comparable and refer to equal numbers of disintegrating atoms.

Before considering these results in more detail we wish to draw attention to the two γ -rays 13.90×10^6 volts and 14.26×10^6 volts. In the natural β -ray spectrum of radium C there are three easily measurable β -ray lines whose energies agree with those to be expected if a γ -ray of energy 14.26×10^6 volts were internally converted in the K, L_I and M_I states respectively. Further the intensities of these groups would lead one to expect such a γ -ray to appear prominently in the emission spectrum. Thibaud* was the first to remark that no evidence of this γ -ray could be obtained from the spectrum of the electronic groups liberated from ordinary metals when the γ -rays of radium C passed through them. We paid especial attention to this point, and were also unable to find any excited groups which could be associated with such a γ -ray. Supposing it were emitted with a very small intensity

* Thibaud, 'Thèse,' Paris, 1925.

then the relative intensity in column IV would be less than 0.3, and the value of $\frac{\kappa\alpha_r}{1-\alpha_r} \cdot \frac{1}{\tau_K}$ in column V would be greater than 0.5. We have not made these entries in the table, since we wish to emphasise that there is no direct evidence from our experiments that such a γ -ray is ever emitted. We can, however, infer that a quantum switch of magnitude 14.26×10^5 volts occurs in the nucleus, but that for some reason it does not lead to the emission of a detectable amount of radiation. We shall defer the discussion of this interesting point to another occasion.

While searching for evidence of this γ -ray in the excited spectrum we observed a somewhat faint group which at first appeared to be almost in the correct place. Careful measurements showed, however, that it was due to a γ -ray 13.90×10^5 volts which had not previously been noticed in the radium C spectrum. No corresponding groups in the natural β -ray spectrum of radium C had been previously recorded, and it became a matter of great importance to see whether such groups were present, or whether we had here a phenomenon just the inverse of that presented by the quantum switch 14.26×10^5 volts. After a very careful search we were able to find the corresponding natural group due to conversion in the K level which showed that there was no abnormality in the case of this γ -ray. It was easy to see how this line could have been missed in previous investigation of this spectrum, since unless a long exposure was given under conditions just suited for this line it became very difficult to detect in the tail of the strong natural group due to the 14.26×10^5 volts nuclear switch.

The last column of Table I contains the values of $\frac{\kappa\alpha_r}{1-\alpha_r} \cdot \frac{1}{\tau_K}$ and to obtain from this the actual value of the internal conversion coefficient we need information about the photoelectric absorption coefficient in this region. Unfortunately no direct determination of this quantity has been made at these high frequencies; Allen* extended his measurements to just over 100,000 volts and we know of no other attempt to go to higher frequencies.

It is well known from the work of J. A. Gray† and others that a continuation of the approximate X-ray law $\tau \propto \lambda^3$ cannot be valid at high frequencies, in fact for γ -rays of about one million volts the dependence of τ on λ follows more nearly a square law. The recent measurements of Skobelzyn‡ of the intensity

* Allen, 'Phys. Rev.', vol. 27, p. 266 (1926).

† Gray and Cave, 'Trans. Roy. Soc. Canada,' vol. 21, p. 163 (1927).

‡ Skobelzyn, 'Z. Physik,' vol. 43, p. 354 (1927), and vol. 58, p. 595 (1929).

distribution in the γ radiation of radium (B + C) make it possible, however, to test any proposed empirical formula against the known absorption in lead and aluminium. We are greatly indebted to Mr. L. H. Gray for help in this matter.

As a convenient empirical formula he took $\log_{10} \tau = a + b \log_{10} \lambda + c (\log_{10} \lambda)^2$. In effect two of the constants are determined by arranging that this expression joins on both as regards magnitude and slope to Allen's measurements, and the third can be adjusted to give the best fit with the absorption measurements. From a careful consideration of the available data Mr. Gray concludes that b and c should have values of about 1.00 and 0.480 respectively. The values of τ given by this empirical formula appear, if anything, to diminish rather too rapidly with increasing frequency.

For reduction of our results we require that portion of the photoelectric absorption coefficient which refers to conversion in the K level. We have assumed that the K jump for platinum has a value 5.3 and hence obtain the values shown in column II of Table II. There is another use we can make of these values of τ_K . By division by τ_K of the quantities shown in column IV of Table I we obtain relative values of $p_r(1 - \alpha_r)$ that is relative values of the intensities of the emitted γ -rays.

Table II.

Col. I.	Col. II.	Col. III.	Col. IV.
$h\nu$ of γ -ray in volts $\times 10^{-3}$.	τ_K photoelectric absorption coefficient in K level of platinum.	$\frac{\kappa_r^a}{1 - \alpha_r}$,	$p_r(1 - \alpha_r)$ number of quanta emitted per disintegration.

Radium B.

2.43	9.00	0.364	0.115
2.97	5.35	0.186	0.258
3.54	3.45	0.117	0.450

Radium C.

6.12	0.940	0.0061	0.658
7.73	0.568	0.0048	0.065
9.41	0.370	0.0061	0.067
11.30	0.256	0.0062	0.206
12.48	0.210	0.0057	0.063
13.90	0.170	0.0014	0.064
14.26	0.162	—	—
17.78	0.108	0.0016	0.258
22.19	0.073	0.0013	0.074

Mr. L. H. Gray has recently made a redetermination by a new method of the total energy emitted in the form of γ -rays by the radium B and radium C in equilibrium with 1 gram of radium, and finds a value about 9.2 calories per hour. We shall obtain an upper limit to the absolute intensities, that is the average number of quanta emitted per disintegration, if we consider this energy to reside entirely in the γ -rays shown in Tables I and II. Proceeding in this way we obtain the figures shown in column IV of Table II. Although the exact figure cannot be settled with certainty it seems likely that this method of obtaining the absolute intensities will overestimate the values by about 10 per cent.

Before discussing the significance of these results it is convenient to point out a slightly different meaning which might be attached to these measurements. If we consider an excited nucleus which is capable of making a switch of energy $h\nu$ we know that several different occurrences may result. A quantum of radiation may be emitted, or an electron from the K-, L-, M-levels. From analogy with the well-known presentation of dual decay we might attempt to describe this by giving the branching ratios. The radiation branch is usually the most prominent and it is convenient to give the frequency of occurrence of the other branches with reference to this mode. On this view ${}_K\alpha_r/(1 - \alpha_r)$ measures the branching ratio of the ejection of the K electron, ${}_L\alpha_r/(1 - \alpha_r)$ that of ejection of the L electron, and so on, and the internal conversion coefficient does not appear as an independent quantity. In this case the quantity which determines the absolute frequency of occurrence is the average number of switches per disintegration, that is the quantity p_r . This can easily be deduced from the values given in Tables II and III (*infra*). Except for the radium B γ -rays it is practically identical with $p_r(1 - \alpha_r)$.

To complete the presentation of our experimental results we include—in Appendix II our values of the relative intensities of the groups in the natural β -ray spectrum of radium B and radium C. These have been measured previously by Ellis and Wooster,* and on the whole our results are in good agreement. The final values differ since we have used the experimentally determined correction factor† for the dependence of photographic action on velocity of the β particle instead of the $1/\beta^2$ law assumed by Ellis and Wooster. From this table it is at once possible to deduce the ratios of the internal conversion coefficients for a given γ -ray in the different states, that is, for example, ${}_L\alpha_r/{}_K\alpha_r$, since this is given by the ratio of the intensities of the corresponding

* Ellis and Wooster, 'Proc. Roy. Soc.,' A, vol. 114, p. 276 (1927).

† Ellis and Aston, 'Proc. Roy. Soc.,' A, vol. 119, p. 645 (1928).

Table III.—Ratio of the Internal Conversion Coefficients for different levels for certain of the γ -rays of RaB and RaC.

$h\nu$ of the γ -ray in volts $\times 10^{-5}$.	$\frac{I_1^a}{K^a}$	$\frac{M_1^a}{K^a}$	$\frac{N_1^a}{K^a}$
2.43	0.12	0.03	—
2.97	0.13	0.02	—
6.12	0.22	0.04	0.04
11.30	0.16	0.08	—
14.26	0.14	—	—

natural β -ray groups. The results for those γ -rays, which we consider to give both independent and dependable values are collected in Table III. Owing to the small intensities of the L, M, N groups the measurements are bound to be inaccurate, and it is difficult to be sure whether the ratios should be constant or whether the differences are significant. It seems likely, however, that the γ -ray 6.12×10^5 volts gives a value higher than the remainder. From these figures we obtain $\alpha_r/K\alpha_r = 1.24$ since by definition $\alpha_r = K\alpha_r + L\alpha_r + \dots$

The results in these tables go some way towards presenting a quantitative account of the events occurring in a radioactive disintegration. We know now what γ -rays are emitted, approximately how often each is emitted, and how often instead the nuclear switch leads to an ejection of an electron from the outer system of the atom.

§ 5. Discussion.

Gurney has measured directly the number of electrons per disintegrating atom which are emitted in the strong β -ray groups Hp 1410, 1677 and 1938 of radium B due to the γ -rays 2.43, 2.97 and 3.54×10^5 volts respectively. The semicircular focussing method was used to isolate the groups, and by varying the magnetic field each was allowed in turn to enter a Faraday cylinder. His results are shown in column II of the next table. Column III shows the relative intensities of these groups that we have found by the photographic method, and column IV the ratio of the two measurements. It will be seen that they do not agree. In view of this discrepancy we paid special attention to the relative intensities of these groups, and we find it difficult to believe that our results are greatly in error. We can only suggest that since Gurney used a thin glass tube filled with radon as a source of the β -rays of radium B, it is possible that even with the large defining slits employed, the lower velocity groups were so straggled by passage through the glass that they could not

enter completely into the Faraday cylinder at any one setting of the magnetic field.

Table IV.

Col. I.	Col. II.	Col. III.	Col. IV.	Col. V.
H ρ of β -ray group.	Number of electrons per disintegration measured electrically (Gurney).	Relative intensities of groups measured photographically.	Ratio of cols. II and III.	$p_r \cdot \kappa \alpha_r$ calc.
1410	0.024	80	0.00030	0.042
1677	0.039	91	0.00043	0.048
1938	0.053	100	0.00053	0.053

Another estimation of the reliability of our results may be obtained in the following way. We have seen how it was possible to deduce from our measurements both values for the branching ratio between internal conversion and emission of a γ -ray, that is for the quantity $\kappa \alpha_r / (1 - \alpha_r)$, and also values for the number of quanta of each frequency emitted per disintegration, that is for the quantity $p_r (1 - \alpha_r)$. The product of these two quantities is $p_r \cdot \kappa \alpha_r$, which is the number of electrons emitted per disintegration due to the internal conversion of the r th γ -ray. We ought, therefore, to be able to deduce from our experiments the quantities measured directly by Gurney, and already shown in column II of the last table. Our calculated values of $p_r \cdot \kappa \alpha_r$ are given in column V of that table. It will be seen that not only is the order of magnitude correct, which is a matter of some importance when we consider the number of different steps which have led to our final results, but that the agreement is best for the γ -ray 3.54×10^5 volts for which we should anticipate Gurney's measurement to be most reliable. It is difficult to disentangle the various factors which might affect the accuracy of our work, but unless errors have tended to compensate it appears that our theory of the form of the excited line (§ 6) and choice of τ values (external photoelectric absorption coefficient) are in the main correct.

One of the most striking points about the values (see Table II) of the internal conversion coefficients for the different γ -rays is their dependence on the frequency. The values for radium B show a marked decrease with increasing frequency, but the range of frequency is not great. The values for radium C, which extend over a frequency range of three to one, give no indication of a steady variation. Within the experimental error the value of the coefficient is constant for the first five γ -rays, and then drops by a factor of four to another

constant value for the remaining three γ -rays. There is also a large difference in the general order of magnitude of the coefficients for the two bodies, and these two points together raise the important question whether there is a real difference in behaviour as regards internal conversion between radium B and radium C. This is not immediately obvious since the three radium B γ -rays which have been investigated are of considerably lower frequency than the radium C γ -rays, however we think the following arguments show, in the first place, quite definitely that at the same frequency radium C γ -rays have a much lower internal conversion than those of radium B, and in the second place, render it at least a tenable hypothesis that the radium B coefficients decrease with increasing frequency, whereas, except for sudden jumps, the radium C coefficients do not vary with the frequency.

We will consider two rather weak γ -rays, one of 4.71×10^5 volts from radium B, and one of 4.29×10^5 volts from radium C. We have not extended our present measurements to these γ -rays, but they have both been detected by the crystal method by Frilley.* While both γ -rays were of feeble intensity the radium C γ -ray appeared definitely to be the stronger. Now the relative intensities of the β -ray lines due to K internal conversion show just the opposite behaviour, the radium B line being about five times the stronger. It follows therefore that for approximately the same frequency the internal conversion coefficient of the radium B γ -ray is more than five times as great as that of the radium C γ -ray. This is the first point referred to. The second point is admittedly speculative, and is simply that if one extrapolates the variation shown by the three measured values for radium B up to the γ -ray 4.71×10^5 volts, and further assumes that the coefficient for radium C does not change from the last measured value (at 6.12×10^5 volts) down to 4.29×10^5 volts, then one obtains entirely reasonable values of 0.02 and 0.03 quanta per disintegration for the intensities of these two γ -rays.

This distinction between the conversion coefficients of radium B and radium C, certainly as regards magnitude, probably as regards dependence on frequency, appears to us to be an important point and shows definitely that the structure of the nucleus is involved in this problem. The two atoms are, except for the detailed structure of the nuclei, so similar that on general grounds it would appear hopeless to expect an explanation of these phenomena from a model consisting only of a standard γ -ray emitter, situated at the centre of the atom and characterised only by its frequency, and of the normal electronic structure. Important calculations on this basis were carried out some time

* Frilley, 'Thèse,' Paris, 1928.

ago by B. Swirles.* The γ -rays were treated as spherical waves sent out by a vibrating dipole at the centre of the atom and only radiative coupling between the nucleus and electronic system was assumed. As was to be expected from a radiation hypothesis the coefficient was found to vary with the frequency according to a power between 2 and 3.5, which while possibly in agreement with the radium B variation, could not account for the radium C results. An even more fundamental disagreement, however, appeared in the magnitude of the calculated coefficient. Briefly the calculation gives too small a value both for radium B and radium C, and in so far as it is possible to compare two quantities varying differently with frequency, the discrepancy was of the order of a factor of 10.

In face of these facts we have no hesitation in abandoning the hypothesis of only radiative coupling between the nucleus and electronic system, in fact our results point directly to a direct action of the nucleus on the electronic structure. By this we mean that as regards this phenomenon the constituents of the nucleus and the outer electronic structure are in contact and capable of collision interaction in much the same way, if not to the same extent as are the K, L and M electrons. It is scarcely necessary to point out that such an interaction would be expected on the wave mechanics. Any quantum-mechanical system in the nucleus, even if situated behind a potential barrier, would be capable of direct interaction with the electronic system owing to the spread of the wave functions. This problem is discussed in detail in a following paper by R. H. Fowler. The interesting point emerges that if the γ -rays are considered to be emitted by transitions of an α -particle between two stationary states, which is certainly the simplest assumption, the calculated values of the conversion coefficients are still far too small. It appears that the peculiarities of this phenomenon have their cause in the detailed structure of the nucleus and of the system which emits the γ -rays, and it is to be hoped that a close study of internal conversion will lead to important information.

The radiation hypothesis of internal conversion fails most drastically in the case of the nuclear switch of 14.26×10^6 volts. While this transition gives rise to strong electronic groups the corresponding radiation has never yet been uniquely observed. Mr. Fowler has pointed out to us that a natural interpretation of this behaviour is obtained if the nuclear transition is assumed to be one that is forbidden by some selection rule, for example the azimuthal quantum numbers of both levels might be zero. This restriction would, of

* B. Swirles, 'Proc. Roy. Soc.,' A, vol. 116, p. 491 (1927); vol. 121, p. 447 (1928).

course, not apply to interaction with the other electronic structure of the type we have discussed.

The second aim of this work was to determine the intensities of the γ -rays. Skobelzyn* has also investigated this problem but by an entirely different method, and the measurements can only be compared if due regard is paid to the distinctive features of the two experiments.

The method we have used, which we will term the photoelectric method, was to compare the intensities of the β -ray groups due to the photoelectric conversion of the γ -rays in platinum. It is only applicable to the more intense γ -rays and becomes rapidly less sensitive for higher frequencies due to the rapid decrease in amount of the photoelectric absorption. It has, however, one important advantage, the intensity of each γ -ray that can be detected is determined independently of neighbouring weak γ -rays or any continuous γ -ray emission. We have described how the β -ray groups were always superimposed on a general background due to recoil electrons liberated from the platinum. The method of isolating the line was to measure this background both in front of and behind the line and then to interpolate for its value throughout the line. This method will also separate the effect of an intense monochromatic γ -ray from the photoelectric effect of both continuous γ -radiation and weak monochromatic γ -rays, since, in the latter case, if the γ -ray is not sufficiently intense to give a measurable hump on the plate its effect is attributed automatically to the background. The photoelectric method, while limited in its application to the stronger rays, has therefore the great advantage of selectivity.

Skobelzyn utilised the Compton effect to study the relative intensities of the γ -rays of radium B and C. A narrow pencil of γ -rays was allowed to pass horizontally through an expansion chamber, and a magnetic field was applied perpendicular to the plane of the chamber. The tracks of the recoil electrons were thus curved and a measurement of this curvature and of the angle of ejection determined the frequency of the γ -ray responsible for the scattering process. Only recoil tracks making an angle of less than 20° with the direction of the ray beam were considered and the Klein-Nishina† scattering formula shows that to a close approximation the number of such tracks for constant intensity of the γ -ray is independent of the frequency of the γ -ray. A study of the relative number of recoil tracks of different speeds therefore gave directly the relative number of quanta of different frequencies. The two advantages

* Skobelzyn, 'Z. Physik,' vol. 43, p. 354 (1927), and vol. 58, p. 595 (1929).

† Klein and Nishina, 'Z. Physik,' vol. 52, p. 853 (1928).

of this method are, firstly, that it is equally sensitive to high frequency γ -rays as to low; in fact, the method tends to be rather more accurate for high frequency γ -rays where the recoil electrons are faster. Secondly, it detects and measures the intensities of the weak γ -rays just as efficiently as it does the more intense γ -rays. The one disadvantage is that the resolution is not high and the effects of different γ -rays cannot be easily separated. The frequency of the γ -ray responsible for any one recoil track cannot be determined with an accuracy much greater than 5 per cent. so that in the final results homogeneous γ -rays appear as broad bands.

It will be seen that these two methods are complementary; Skobelzyn's method should give an accurate picture of the general spectral distribution without being able to give the relative intensities of the individual γ -rays. On the other hand the photoelectric method is specially suited for this latter point, but is insensitive to the weaker γ -rays and to the higher frequency γ -rays. We should not expect to be able to effect a close comparison between the results of these experiments, but it is important to see that they are not incompatible. Skobelzyn's measurements are shown in fig. 2 plotted against the quantity $H\rho_{\max}$.^{*} This is the $H\rho$ the recoil electron would have if ejected straight forward in the direction of the γ -ray beam. In the region we are concerned with $H\rho_{\max}$ is practically a linear function of the frequency of the γ -ray. The ordinates show the number of tracks falling in an interval of 100 $H\rho_{\max}$ which is equivalent approximately to 0.3×10^6 volts frequency change. Since the average number of tracks in the intervals chosen by Skobelzyn was about 10 to 20 it is clear that the probability error is large. Remembering further that owing to the experimental errors in measuring the tracks a homogeneous γ -ray will show as an error curve with a half breadth of about 2 to 3 per cent. we see that this curve can be mainly accounted for by a series of monochromatic γ -rays. On the same diagram we have marked the position of the γ -rays we have measured, the heights of the lines showing the intensities. The agreement between the peaks on the curve and the positions of the strong γ -rays is most striking. Taking into account that there are many weaker γ -rays which will have been measured by Skobelzyn we see that it is unlikely

^{*} Skobelzyn presents his results by giving the actual number of tracks observed to fall within certain $H\rho_{\max}$ intervals. While this is an unambiguous way of recording the measurements we think the present method is better suited to our immediate purpose. It is, however, important to note that the statistical error of any point on the curve must be taken from the original measurements and cannot be deduced from the corresponding ordinate of fig. 2.

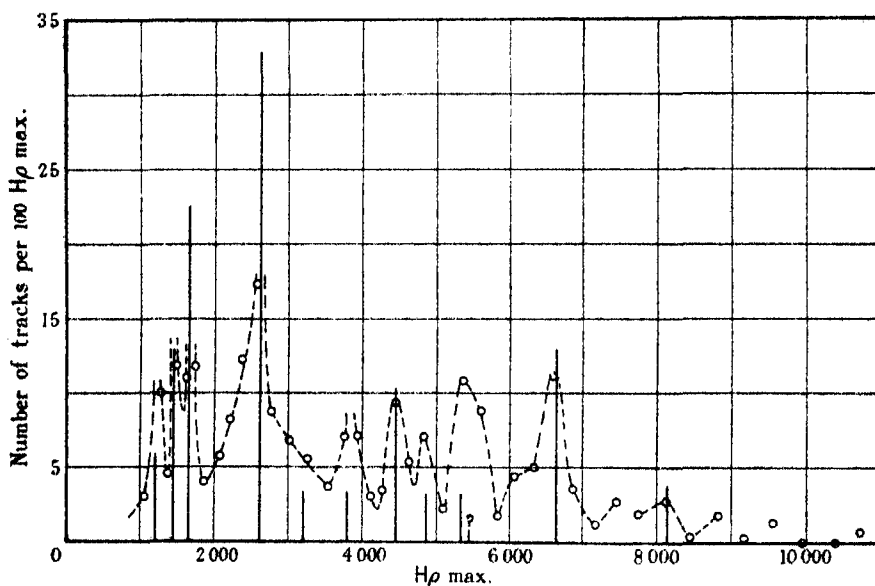


FIG. 2.

that much energy is emitted in the form of continuous γ -radiation. Two further points call for notice. The detection of a small number of tracks with $H\rho_{\text{max.}}$ as great as 10,000 shows that radium C emits γ -rays of frequency as high as 3.0×10^6 volts. These would be extremely difficult to detect by the photoelectric method, but even if such γ -rays have a small intensity they will contribute markedly to the total energy emitted. It is this fact, coupled with the undoubted emission of weaker γ -rays throughout the spectrum, which shows that in deducing the absolute intensities of the strong γ -rays by ascribing to them the total energy emission we overestimate their intensities by at least 10 per cent.

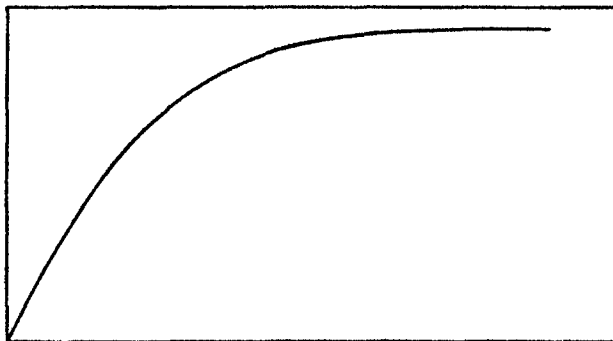
Considering the accuracy of each of the two methods the values of the intensities may provisionally be held to be compatible. In Skobelzyn's experiment the γ -rays were filtered through 3.5 mm. of lead and 2 mm. of glass which will have reduced perceptibly the intensities of the softer γ -rays. There is, however, a marked discrepancy in the region 14.0×10^5 volts where the Compton effect method indicates a relatively strong emission, more than can be accounted for by the intensity of the one γ -ray 13.89×10^5 volts found by the photoelectric method. It is of course just possible that both measurements are considerably in error in opposite directions, and it might be possible to reconcile them. The reconciliation would be helped if a γ -ray 14.26×10^5

volts were really emitted, but with an intensity so small as to escape detection by the photoelectric method. There is not enough evidence at present to settle this very interesting question and we must await further experiments by the Compton effect method.

APPENDIX I.

§ 6. *The Theory of the Shape of the Excited β-ray Lines.*

We will discuss at first a simplified case in order that the main factors involved may be made clear. We confine our attention to the electrons ejected from the K level by one particular homogeneous γ-ray, and we assume that the surface emission of these electrons is isotropic. It will be shown later from the results of White and Millington* that, neglecting scattering, the effect of straggling on the electrons from the lower layers of the platinum is to make the number of electrons which have been retarded by an amount between $\Delta H\rho$ and $\Delta H\rho + d(\Delta H\rho)$ independent of $\Delta H\rho$. This should produce a line on the plate of the shape shown in fig. 3, but actually the line is of the shape



* FIG. 3.

shown in fig. 1b. It is clear that the reason for this is that some effect such as scattering has reduced the number of electrons which have lost large amounts of energy, so that the number of electrons which have lost between $\Delta H\rho$ and $\Delta H\rho + d(\Delta H\rho)$ is a continuously decreasing function of $\Delta H\rho$.

It is convenient here and in future to use x , the distance along the plate from the high velocity foot of the line, as parameter instead of $\Delta H\rho$. If the radius of curvature of the path of the electrons in a field of H gauss is ρ cm. and x is measured in millimetres then to a first approximation

$$x = 20\Delta H\rho/H = 20\Delta H\rho \cdot \rho/H\rho.$$

* White and Millington, 'Proc. Roy. Soc.,' A, vol. 120, p. 701 (1928).

We will now consider how an excited line as in fig. 1b could arise from a source emitting electrons with a velocity distribution $a(x)$ [$a(0)$ being unity], under the extra condition that homogeneous electrons from such a source give a line of the form shown in fig. 1a.

The electrons of each particular velocity will produce a line of the same form as the natural line but displaced by an appropriate amount corresponding to the difference in velocity. The excited line may be regarded as being built up by the superposition of a series of such lines, and a particular ordinate of the excited line will be equal to the sum of the ordinates at the same value of x of the displaced lines corresponding to the electrons of various velocities. Let $e(x)$ represent the excited line and $v(x)$ the natural line, each for an exposure of one milligram-hour. Then

$$e(x) = B \int_0^x a(z) v(x-z) dz,$$

where B is a constant depending on the relative intensities of the natural and excited lines. Hence the area of the first M mm. of the excited line is

$$\int_0^M e(x) dx = B \int_0^M dx \int_0^x a(z) v(x-z) dz,$$

B can be found from the experimental results when $a(x)$ is known. The appropriate form for $a(x)$ can be found by trial and error since it must give the same value of B for the different portions of the excited line. We will suppose B to have been determined in this way and go on to show how from this we can obtain a relation between α and τ .

The electrons forming the natural and excited lines are of practically the same velocity so their photographic effects will be identical. If we therefore consider the photometer curves of the natural and excited lines, corrected for the characteristic curve of the plate, i.e., $v(x)$ and $e(x)$, the ratio of the area of the natural line to the number of electrons which contribute to it will be the same as the ratio of the first M mm. of the excited line to the number of electrons which contribute to the M mm. We shall therefore calculate these two ratios and equate them.

The ratio for the natural line can be written down at once. The area is $\int_0^d v(x) dx$ where d is the length of the line, and the number of electrons contributing to the line is $\frac{1}{2}P \cdot p \cdot x \alpha \cdot \frac{\omega}{4\pi}$, where P is the number of disintegrating

per milligram-hour and ω is the solid angle to which the electrons are limited by the slit. Hence for the natural line the ratio is

$$8\pi \int_0^d v(x) dx / P \cdot p \cdot \kappa \alpha \cdot \omega. \quad (1)$$

Let the number of electrons with velocities corresponding to values of x between x and $x + dx$ which contribute to the excited line be $N a(x) dx$. Of these a fraction

$$\int_0^{M-x} v(y) dy / \int_0^d v(y) dy$$

can get into the first M mm. of the excited line. Hence the total number of electrons getting into the first M mm. of the excited line is

$$N \int_0^M a(x) dx \int_0^{M-x} v(y) dy / \int_0^d v(y) dy. \quad (2)$$

As shown above the area of the first M mm. of the excited line is

$$B \int_0^M dx \int_0^x a(z) v(x-z) dz,$$

which can also be written

$$B \int_0^M a(x) dx \int_0^{M-x} v(y) dy. \quad (3)$$

Hence the ratio for the excited line is obtained by dividing expression (3) by expression (2) and equals

$$\frac{B}{N} \int_0^d v(y) dy. \quad (4)$$

Equating (1) and (4) we thus obtain

$$\frac{8\pi}{P \cdot p \cdot \kappa \alpha \cdot \omega} = \frac{B}{N}. \quad (5)$$

It will be shown later how the number of electrons N which occurs in this equation can be calculated from the number n liberated per unit volume by considering the effect of straggling on the electrons coming from the lower layers; n involves directly the intensity of the γ -ray, i.e., $p(1-\alpha)$, τ and P while ω also appears in the expression for N so equation (5) gives a relation between α and τ in terms of the experimental quantities, namely the dimensions of the tube, the straggling coefficients and the relative intensities of the natural and excited lines.

We must now consider the effects of certain other factors. The emission from the tube is not isotropic as we have assumed but in general would have to be described by a function $m(\theta) a_\theta(x)$, [$a_\theta(0)$ being unity], giving the number and velocity distribution of the electrons going through the slit from each point (defined by an angle θ) on the surface of the source. We can easily see how the lack of uniformity arises. The photoelectrons ejected by the γ -rays are not uniformly distributed in space. The number of electrons passing through the slit from each part of the surface layer of the source will be determined by the probability of photoelectric emission in the required direction, but electrons liberated in the lower layers may have their directions altered as a result of scattering in the platinum.

Now we found experimentally that the form of the excited line was practically the same for all the γ -rays, a result that was no doubt due to mutually compensating changes in $m(\theta)$ and $a_\theta(x)$. It would be extremely complicated to attempt to follow this out in detail, so we assumed that the same values of $m(\theta)$ and $a_\theta(x)$ would apply to all the lines, since this clearly satisfies the experimental result. It will be seen later that $m(\theta)$, the initial ordinate of the velocity distribution curve of the electrons from each point of the source, can be calculated with fair accuracy. In the comparison of the natural and excited lines we therefore did not use the true form of the natural line, but the form one would obtain if the density of the radioactive material on the source varied as $m(\theta)$. Under these conditions we thought it sufficiently accurate to use the same velocity distribution function for all portions of the source. The error introduced in this way is unlikely to be serious since we determine an arbitrary distribution to fit the experimental results, and it does not appear explicitly in the final formula.

With these simplifications it is now possible to carry through the same argument as before, but we make it applicable to any line by taking into account the fact that they were always photographed at the same radius of curvature ρ (a small correction being applied when this was not so), and by expressing the intensities of the natural and excited lines in terms of the corresponding lines due to the γ -ray of energy 3.54×10^6 volts. If the peak intensities of the natural and excited lines respectively due to the r th ray are respectively L_r and G_r , and B is found for the standard γ -ray, then in the equation for the r th γ -ray we shall have to put $G_r B / L_r$ in place of B . In place of equation (5) above we then have

$$\frac{8\pi}{P \cdot p_r \cdot \kappa^2 \cdot \omega} = \frac{G_r \cdot B}{L_r \cdot N} \quad (6)$$

It remains now to find the value of N which it will be remembered has the meaning that $N a(x) dx$, ($a(0) = 1$) electrons leave the source in such directions as to be able to contribute to the line, and which have been so diminished in velocity that they strike the plate between x and $x + dx$ behind the front edge of the line.

The value of N depends largely on the extent of the straggling the electrons suffer in emerging from the platinum. Disregarding any reduction in the number of electrons White and Millington* showed that for mica the number of electrons which have lost between $\Delta H\rho$ and $\Delta H\rho + d(\Delta H\rho)$ due to passage through a thickness t was $g\left(\frac{\beta^3}{t} \cdot \Delta H\rho\right)$ where $g(z)$ was a function for which they gave numerical values. Millington confirmed that the same result held for gold. The function $g(z)$ is zero for $z < a$ and $z > b$ where a and b are characteristic constants of the material. We will now consider a simple case, that of the velocity distribution of the electrons issuing from a slab of material in which there is a production of k electrons per unit volume per second ejected in the forward direction, and we will also neglect any reduction in the number of electrons due to absorption. The number of electrons per unit area from a layer dt at a distance t below the surface which have lost between $\Delta H\rho$ and $\Delta H\rho + d(\Delta H\rho)$ is $kdt \cdot \frac{\beta^3}{t} g\left(\frac{\beta^3}{t} \cdot \Delta H\rho\right) d(\Delta H\rho)$. Hence the total number of electrons from all depths which have lost between $\Delta H\rho$ and $\Delta H\rho + d(\Delta H\rho)$ is

$$Y(\Delta H\rho) d(\Delta H\rho) = k d(\Delta H\rho) \int_{\frac{\beta^3}{b} \Delta H\rho}^{\frac{\beta^3}{a} \Delta H\rho} \frac{\beta^3}{t} g\left(\frac{\beta^3}{t} \Delta H\rho\right) dt.$$

The limits of the integral are determined by the fact that only thicknesses between t_1 and t_2 can contribute where $a = \frac{\beta^3}{t_1} \Delta H\rho$ and $b = \frac{\beta^3}{t_2} \Delta H\rho$. Introducing a new variable $q = \frac{\beta^3}{t} \cdot \Delta H\rho$ the integral becomes

$$Y(\Delta H\rho) d(\Delta H\rho) = k d(\Delta H\rho) \beta^3 \int_a^b \frac{1}{q} g(q) dq = k d(\Delta H\rho) \beta^3 \cdot S,$$

where S is a constant of the material and independent of the velocity, which can be evaluated from the standard straggling curve $g(z)$. The term β^3 in this expression is exactly equivalent to the similar term in the well-known

* White and Millington, 'Proc. Roy. Soc.,' A, vol. 120, p. 701 (1928).

result that the mean retardation of a beam of electrons in passing through a sheet of matter is inversely proportional to β^3 . This latter result is not exact and the necessary correcting factor $f(\beta)^*$ with which β^3 must be multiplied is given by Bohr's† theory. We have assumed that the same correcting term applies here and write the above equation

$$Y(\Delta H\rho) d(\Delta H\rho) = kd(\Delta H\rho) \beta^3 f(\beta) \cdot S.$$

This equation shows that the distribution curve would be a straight line parallel to the axis of abscissa $\Delta H\rho$, the result of assuming there is no reduction in the number of electrons. If we consider absorption we should have to multiply the contribution from the layer at depth t by a $F(t)$ less than unity where $F(0) = 1$. On changing the variable to q this would become $F(\beta^3 \Delta H\rho/q)$, and it is seen that the initial ordinate $Y(0)$ of the distribution curve will be unchanged. This is precisely the case we require since the quantity N is the initial ordinate of the velocity distribution curve. However, in the application of this result to the platinum tube we must take into account that although the γ -rays are confined mainly to the radial direction the electrons are not all emitted in the forward direction. We will assume that it is sufficiently accurate to take a single function $I(\theta)$ to represent the probability of ejection in unit solid angle of electrons at an angle θ to the radius. Further let n represent the total number of electrons produced per cubic centimetre by the particular γ -ray during the entire standard exposure of 1 milligram-hour. If we neglect scattering the number of electrons crossing a small portion of the surface of the tube of area dA in directions between θ and $\theta + d\theta$ from the normal after traversing a distance t in the platinum is (see fig. 4a)

$$nt d\theta \cdot dt \cdot 2\pi t \sin \theta \cdot t^{-2} dA \cos \theta \cdot I(\theta) = 2\pi n \sin \theta \cos \theta \cdot I(\theta) d\theta \cdot dt \cdot dA.$$

We require the number of electrons going into a solid angle ω where this is the solid angle of the effective beam of electrons limited as described above by the

$$* f(\beta) = \frac{1}{96 \cdot 1 - \log Z/A + \log_e \sigma - \log_e \frac{1 - \beta^2}{\beta^2} - \beta^2 - 2C}$$

where Z is the atomic number, A the atomic weight, σ the thickness in centigrams per square centimetre and C the characteristic constant of the material. The general evidence indicates that this correction will not depend markedly on the nature of the material so we have inserted the values for mica which is the only substance which has been closely investigated. The thickness was taken proportional to $H\rho$ and of value 8 mg./cm.² for $H\rho$ 1990.

† Bohr, 'Phil. Mag.' vol. 25, p. 10 (1913), and vol. 30, p. 581 (1915).

slit and the width of the trace on the photographic plate. Owing to the small size of the source compared with its distance below the slit ω is independent

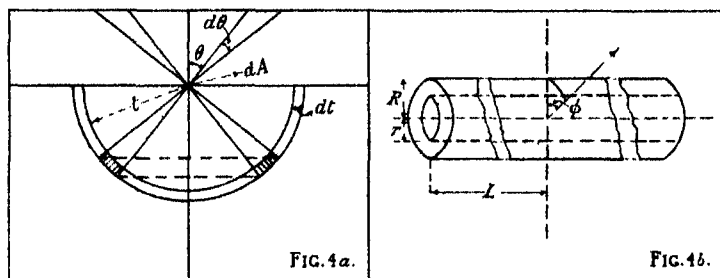


FIG. 4.

of θ . The number of electrons going into the solid angle ω is therefore obtained by multiplying by $\omega/2\pi \sin \theta d\theta$ and is

$$\omega n \cos \theta . I(\theta) dt . dA .$$

Considering now the straggling of these electrons we see that the initial ordinate of the velocity distribution curve plotted against $\Delta H\rho$ is

$$\omega n \cos \theta . I(\theta) dA \beta^3 f(\beta) . S .$$

If we change from $\Delta H\rho$ to the quantity x representing the distance in millimetres behind the foot of the line, and further measure all distances in the platinum in milligrams per square centimetre the above expression becomes

$$\frac{\omega n \cos \theta . I(\theta) dA \beta^3 f(\beta) S . (H\rho)}{4.3 \times 10^6 . \rho} .$$

To obtain N we now substitute $R . d\phi . dL$ for dA (see fig. 4b) and integrate over the source from $+L$ to $-L$ and $+\pi/2$ to $-\pi/2$. To a fair approximation $d\phi = d\theta$ hence

$$N = \frac{\omega n . H\rho . \beta^3 . f(\beta) . S . 4L . R}{4.3 \times 10^6 \rho} \int_0^{\pi/2} I(\theta) \cos \theta d\theta .$$

The quantity n involves only geometrical factors and the amount of absorption of the γ -ray and is given by

$$n = P . p_r (1 - \alpha_r) \kappa \tau_r . \frac{1}{4\pi^2 L} \int_0^\pi d\theta \int_0^L \frac{dL}{R^2 + r^2 + L^2 - 2r R \cos \theta} .$$

Here P is the number of disintegrations in the standard exposure of 1 milligram-hour, $p_r (1 - \alpha_r)$ the intensity of the r th γ -ray, and $\kappa \tau_r$ the photoelectric

conversion coefficient in the K level. For $I(\theta)$ the angular distribution of the photoelectrons, we took Carrelli's* formula meaned from $\theta + 20^\circ$ to $\theta - 20^\circ$, since the radioactive deposit producing the γ -rays is not located along the axis of the tube but on the inside surface of the cylinder. We have in the previous simplification assumed that $I(\theta)$ is independent of the frequency of the γ -ray. This is not quite accurate but Carrelli's expression is not very sensitive to velocity and the meaned expression still less.

We pointed out earlier that in effecting the comparison between the natural and excited lines the form of natural line taken was calculated for a distribution of radioactive material similar to the surface activity of the excited source. It will be seen now from the above analysis that the appropriate distribution is $I(\theta) \cos \theta$.

If the full expression for N is substituted in (6) the quantities P , p_r and ω cancel out and we obtain after re-arrangement the final result

$$\frac{\kappa \alpha_r}{1 - \alpha_r} \cdot \frac{1}{\kappa \tau_r} = \frac{8}{4.3 \times 10^5 \pi \rho} \cdot \frac{L_r}{G_r} \cdot \frac{H \rho \cdot \beta^3 f(\beta) \cdot S}{B} \int_0^{\pi/2} I(\theta) \cos \theta d\theta \\ \times \int_0^\pi \left(\frac{d\theta}{\sqrt{1 + \frac{r^2}{R^2} - \frac{2r \cos \theta}{R}}} \cdot \tan^{-1} \frac{1}{\sqrt{\frac{R^2}{L^2} + \frac{r^2}{L^2} - \frac{2rR \cos \theta}{L^2}}} \right).$$

This formula shows that to find the internal conversion coefficient α we need to measure the relative peak intensities L_r and G_r of the natural and excited lines and in addition to determine the quantity B . The value of B was obtained from the four main β -ray lines using the mean form of these lines.

APPENDIX II.

Relative Intensities of the Groups in the Natural β -ray Spectra of Radium B and Radium C.

The values for radium B and radium C are on the same scale and refer to equal numbers of atoms disintegrating. The absolute values, that is the number of electrons emitted in each group per disintegration, can be obtained approximately by multiplying these intensities by 5.3×10^{-4} .

* Carrelli, 'Z. Physik,' vol. 56, p. 694 (1929).

Radium B.

H ρ .	Intensity.	H ρ .	Intensity.	H ρ .	Intensity.	H ρ .	Intensity.
660.9	17	855.4	2	1410	80	2015	12
667.0	5	860.9	5	1496	3.9	2064	2.1
687.0	1	877.8	1.5	1576	2.1	2110	1.5
768.8	11	896.0	1.5	1677	91	2256	16
793.1	8	926.2	3	1774	10	2307	8
799.1	4	949.2	3	1832	2.5	2321	1.5
833.0	2	1155	2	1850	0.5	2433	1.5
838.0	5	1209	1	1938	100	2480	1.5

Radium C.

H ρ .	Intensity.	H ρ .	Intensity.	H ρ .	Intensity.	H ρ .	Intensity.
1379	0.1	3145	0.5	5532	0.16	7380	0.18
1438	0.1	3203	0.5	5775	0.17	7530	0.04
1557	1.0	3271	1.7	5904	4.76	7690	0.04
1594	0.2	3307	0.3	5948	0.2	7974	0.04
1834	0.2	3326	0.3	6030	0.2	8090	0.04
1912	0.1	3584	0.6	6161	0.70	8313	0.04
2085	0.5	3824	0.4	6212	0.26	8617	0.18
2156	0.1	4196	0.77	6350	0.07	8885	0.04
2256	0.3	4404	0.5	6523	0.05	9165	0.04
2390	0.1	4866	2.42	6650	0.05	9425	0.04
2550	0.1	4991	0.2	6800	0.05	9655	0.04
2720	0.2	5136	0.4	6932	0.13	10020	0.04
2840	0.1	5178	0.2	6998	0.13		
2890	0.1	5281	0.68	7109	0.79		
2980	7.6	5428	0.16	7240	0.06		

We are very grateful to Prof. Sir Ernest Rutherford, P.R.S., for his constant encouragement and advice during the course of this work. We also wish to thank Mr. G. R. Crowe for help in the preparation of the radioactive sources.

We acknowledge gratefully a grant to one of us from the Government Grant Committee of the Royal Society which has defrayed part of the costs of the research, and also the help we have received from Messrs. Ilford, Ltd., in the preparation of the special photographic plates used.

The Hyperfine Structure of Some Lines in the Arc and First Spectrum of Indium.

By Prof. J. C. McLENNAN, F.R.S., and ELIZABETH J. ALLIN, M.A.*

(Received July 23, 1930.)

This investigation of lines in the arc and first spark spectrum of indium was undertaken with the purpose of evaluating, if possible, the nuclear moment of the indium atom. As far back as 1922 Uhler and Tanch† had studied the structure of some lines in the ultra-violet, but their results did not seem to admit of an interpretation based on a quantum number "I."

In the present investigation the spectra were excited in stages as in the earlier work with thallium‡ by altering the pressure of the vapour in the discharge tube. The analysing apparatus was also the same as that previously employed, namely, a 45 plate high power echelon spectrograph. Ilford "Soft Gradation" plates were used with exposures of 15 minutes to half-an-hour.

Only three strong lines lying in the region that we were able to study had been identified as belonging to the spectrum of indium II. These had been classified as the three strongest lines of the multiplet $5s5d\ ^3D_{123} \rightarrow 5s4f\ ^3F^{\circ}_{234}$.§ If, however, we consider the complete multiplet $^3D^1D \rightarrow ^3F^{\circ}\ ^1F^{\circ}$ we should have 11 lines in all. Hence before beginning the study of the fine-structure, lines due to indium II of wave-lengths below 5600 were isolated by excitation methods and their wave-lengths measured. The following lines were shown to belong to the spectrum of indium II.

Table I.

λ in Å.	ν .	Intensity.
4684.6	21340.6	3
4680.9	21357.5	10
4673.4	21391.7	1
4656.6	21468.9	3
4655.5	21474.0	8
4644.4	21525.3	4
4638.0	21555.0	6
3842.4	26018.0	2
3834.9	26068.9	6

* Holder of a National Research Council of Canada Fellowship.

† Uhler and Tanch, 'Astrophys. J.', vol. 55, p. 291 (1922).

‡ 'Proc. Roy. Soc.,' A, *supra*, p. 43.

§ Green and Loring, 'Phys. Rev.,' vol. 30, p. 574 (1927); K. R. Rao, 'Proc. Phys. Soc.,' vol. 39, p. 150 (1927).

These lines are the nine strongest lines of the $D \rightarrow F^{\circ}$ multiplet mentioned above, the two weakest members being still missing. We have :—

	$^3F_4^{\circ}$	$^3F_3^{\circ}$	$^3F_4^{\circ}$	$^1F_3^{\circ}$
$^3D_3$		4684.6 21340.6 (3)	4680.9 21357.5 (10)	4673.4 21391.7 (1)
$^3D_2$	4656.6 21468.9 (3)	4655.5 21474.0 (8)	(4)	4644.4 21525.3
$^3D_1$	4638.0 21555.0 (6)			
$^1D_2$		3842.4 26018.0 (2)		3834.9 26068.9 (6)

The structure of these lines and of the arc lines $\lambda = 4511 \text{ \AA}$ and $\lambda = 4102 \text{ \AA}$ was then studied. The results obtained are given below. The lines $3842 \text{ \AA}$ and $3835 \text{ \AA}$ lying in the region in which the plates were becoming insensitive and also the lines $4673 \text{ \AA}$, $4656 \text{ \AA}$, were too weak to be measured.

On some of the plates each of the components of the arc line $\lambda = 4102 \text{ \AA}$ was double. This is thought to have been due to reversal since this effect was noticeable in cases in which the conditions in the source were such that all lines on the plate were broadened.

It may be observed from Table II that all the lines have either two or three components. This suggests at once that the indium nucleus possesses a moment of momentum of $\frac{1}{2}h/2\pi$. Two objections might be raised. In the first place it might be argued that the triplets, for example, are only the three strongest components of a more complicated pattern. Each of the triplets observed, however, consists of two strong components with the third much weaker, whereas if they were the three strongest components of a more complicated pattern one would expect a more uniform grading off of the intensities. In the second place it might be that the lines observed consist of two or more lines superposed on one another. A number of such strong lines forming the diagonal of a fine-structure multiplet would have presumably separations governed by the Landé interval rule between the levels. Since lines separated by an amount considerably less than half that of the observed lines would be resolved, it scarcely seems possible that more components would not have been apparent.

Table II.

Unresolved line.			Resolved line.		
λ in A.U.	Intensity.	Classification.	$\Delta\lambda$ (A.U.).	$\Delta\nu$ cm. ⁻¹ .	Intensity.
<i>Indium I.</i>					
4511.31	10	$^2P_{\frac{1}{2}} - ^2S_{\frac{1}{2}}$	0.090	-0.439	8
			0.042	-0.025	5
			0	0	10
4101.76	8	$^2P_{\frac{3}{2}} - ^2S_{\frac{1}{2}}$	0	0	10
			-0.053	0.318	8
<i>Indium II.</i>					
4684.6	3	$^2D_3 - ^3F^{\circ}_3$	0	0	10
			-0.263	1.20	5
4680.9	10	$^3D_3 - ^3F^{\circ}_4$	+0.347	-1.59	3
			0	0	10
			-0.082	0.372	8
4655.5	8	$^3D_2 - ^3F^{\circ}_3$	+0.154	-0.712	3
			0	0	10
			-0.144	0.663	10
4644.4	4	$^3D_2 - ^1F^{\circ}_3$	0	0	10
			-0.041	0.190	8
4638.0	6	$^3D_1 - ^3F^{\circ}_2$	0	0	10
			-0.070	0.329	9
			-0.269	1.259	4

Assuming this value of $\frac{1}{2}h/2\pi$ to be correct we would arrive at the following magnitudes for the separations of the different terms.

Table III.

Term.	
$5s^2S_{1/2}$ of indium I	0.234
$5p^2P^{\circ}_{1/2}$..	0.318
$5p^2P^{\circ}_{3/2}$..	-0.205
$5s5d^3D_3$ of indium II	1.96
$5s5d^3D_2$..	1.37
$5s5d^3D_1$..	-0.929
$5s4f^3F^{\circ}_4$..	1.59
$5s4f^3F^{\circ}_3$..	0.73
$5s4f^3F^{\circ}_2$..	-1.25
$5s4f^1f^{\circ}_3$..	1.18

It may be remarked that although the results given by Uhler and Taneh do not seem consistent among themselves, they have observed one line having six components which would not permit the value of $\frac{1}{2}$ for "I." It is hoped to reach more conclusive results by continuing the study of this element with a concave grating.

In conclusion the authors wish to express their thanks to Dr. A. B. McLay for his assistance throughout the investigation and especially in connection with the classification of the lines.

A New Method of Analysis of Groups of Alpha-Rays.—(1) The Alpha-Rays from Radium C, Thorium C, and Actinium C.

By SIR ERNEST RUTHERFORD, P.R.S., F. A. B. WARD, B.A., Goldsmiths' Senior Student, and C. E. WYNN-WILLIAMS, Ph.D., Exhibition of 1851 Senior Student.

(Received August 15, 1930.)

[PLATES 11, 12.]

Introduction.

In a recent paper,* Ward, Wynn-Williams, and Cave have described a method of counting accurately the number of α -particles emitted per second from a radioactive source. This method,—the practicability of which was first shown by Greinacher,†—involves the amplification by means of thermionic valves of the small ionisation current caused by an α -particle in a few millimetres of its path in air. The amplification can be made linear, so that the final current which actuates the recording instrument is proportional to the ionisation produced by the particle in the ionisation chamber. Compared with that produced by an α -particle, the ionisation produced by a β -particle is too small to be recorded under working conditions. In their work on the determination of the number of α -particles emitted per second from a gram of radium, the magnified current was passed through an Einthoven galvanometer, and clear photographic records were obtained when the α -particles were entering the

* 'Proc. Roy. Soc.,' A., vol. 125, p. 713 (1929).

† 'Z. Physik,' vol. 36, p. 364 (1926), and vol. 44, p. 319 (1927).

chamber at a rate of several hundred a minute. Under the conditions of the experiment, the β and γ -radiations were too weak to cause any disturbance, thus enabling the determination to be carried out with accuracy.

For many purposes, however, it is essential to count particles in the presence of strong γ -radiation, and to achieve this end special attention had to be paid to the amplifying and recording system. An account will be given in a later paper by Wynn-Williams and Ward, of the arrangements employed for this purpose, but it suffices to say here that the ions produced by a particle in the detecting vessel should be driven on to the collecting electrode in a time of the order of 10^{-3} sec., and that the process of amplifying and recording should be sufficiently rapid to give a trace in an interval of less than 10^{-3} seconds. For this purpose, a special oscillograph was constructed which has been found to be very effective. With these modifications it has been found possible to count α -particles at the rate of several hundred per minute even in the presence of strong γ -radiation.*

Geiger and Klemperer† have succeeded in modifying the original Geiger point counter so that it, too, is linear, and gives a measure of the ionisation due to a single particle. For some kinds of experiment, this type of counter has definite advantages over the Greinacher type, inasmuch as the ionisation current is magnified several hundred times by collision. The purpose of this paper is to give examples of the utility of the Greinacher method in counting α -particles under different conditions, and to describe a new method for analysing in detail the complexity of the α -rays expelled from certain radioactive bodies.

It will be seen that we have been able in this way to detect the presence of the long-sought-for group of α -particles of short range emitted in the dual disintegration of radium C, although they are present in only about 1 part in 3,000, mixed with the main group of α -particles of range 7 cm. It will also be shown by this method that the α -rays from actinium C are more complex than was previously supposed.

Experimental Method.

Fig. 1 shows the design of the ionisation chamber. The front of the chamber, F_1 , was formed by sheet of mica, of stopping power about 1.2 cm. for α -rays,

* Fränz, working with a Geiger-Klemperer counter, has adopted methods generally similar to those we have found effective for the reduction of the γ -ray disturbance :—*Vide* 'Z. Physik.' vol. 63, p. 370 (1930).

† 'Z. Physik.' vol. 49, p. 753 (1928).

which was thinly sputtered with silver, or covered with thin gold foil ; 2 mm. behind this was the collecting electrode E, which was supported from the earthed guard-ring, G, by a ring of sealing-wax or sulphur, S. The sputtered mica was maintained at a potential of + 240 volts, so that a uniform field of about 1,000 volts/cm. was maintained throughout the chamber. When an α -particle enters the chamber, the ions from 2 mm. of its path are driven by this field on to the collecting electrode. This electrode is connected directly to the free grid of the first valve of the amplifier. The entry of an α -particle into the chamber accordingly raises the potential of this grid by about 10^{-4} volt, and the charge on the grid then leaks away in a time of the order of 10^{-3}

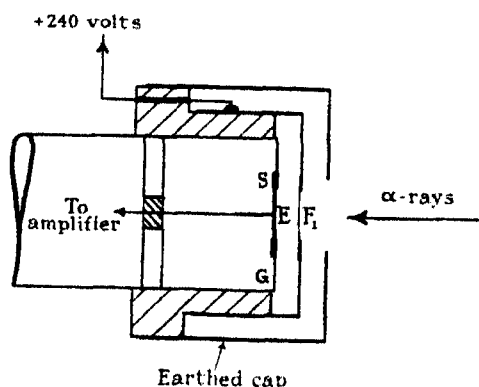


FIG. 1.—Single Chamber Counter.

10^{-2} seconds, depending on the capacity and leak resistance of the insulated grid system. To obtain the maximum peak voltage for a single particle, the capacity should be as small as possible ; hence for the first valve a Marconi V24 or DEV was used, as in these two types the grid lead is brought out to a separate cap. In general, the rest of the amplifier followed normal wireless practice. Extremely careful screening had, however, to be employed, and other points of technical interest had to be attended to ; these will be dealt with in a separate paper to be published shortly. Recording was carried out photographically by means of a moving-iron oscillograph of special design, which will also be described later. The whole amplifying and recording system was linear in characteristic, so that the final deflection of the oscillograph spot was a true measure of the ionisation produced by the particle in the chamber. This linearity is a great advantage, since it means that each deflection recorded is not merely a unit, but an ionisation measurement.

Feather and Nimmo* have investigated the variation of ionisation along the track of an α -particle in air; their method was to photograph the tracks formed by the particles in a Wilson chamber, and to measure the photographic density along the records of the tracks. Their curve is given in fig. 2. It is seen that an ambiguity arises in determining the residual range of an α -particle from the magnitude of the "kick" recorded by the counter, since there are in general two different ranges giving the same ionisation. This difficulty in interpretation is only serious when a very complex α -radiation is being examined, and it is completely eliminated by the differential method of analysis described later.

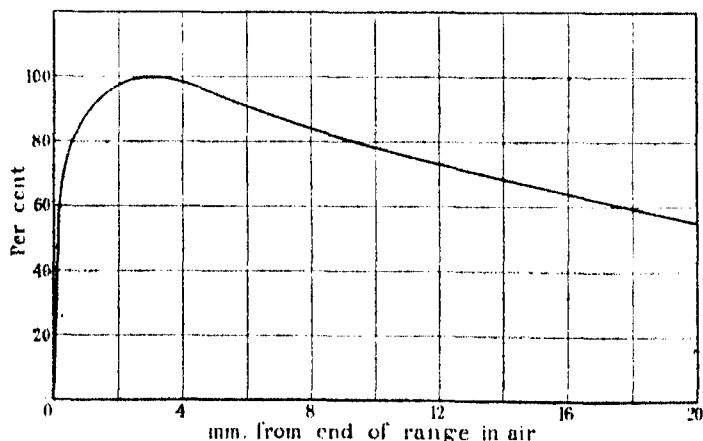


FIG. 2.—Ionisation Curve of Single α -Particle.

As so much of the present work depends upon the linear ratio which exists between the charge given to the first grid, and the deflection of the recording instrument, this relation was investigated very carefully by a series of experiments (to be described in a later paper), and found to hold over the whole of the working range of deflections. A simple experiment, however, illustrates the fact that the deflections of the oscillograph are really ionisation measurements. A very weak source of thorium ($B + C$) on a brass plate was brought up in steps towards the ionisation chamber. Photographs were taken at each step, and the average size of the deflections at each point was measured. When this average size was plotted against the distance from source to chamber, the familiar Bragg ionisation curve

* 'Proc. Camb. Phil. Soc.,' vol. 24, p. 139 (1928).

was obtained. A photograph (fig. 16, Plate 12) is reproduced from a portion of the record obtained when the source was 4 cm. from the chamber. It will be seen that two different sets of kicks are present, the larger ones due to the particles of 4.8 cm. range, which have the peaks of their ionisation curves in the chamber, and the smaller ones due to the 8.6 cm. particles, which are on the lower portion of their ionisation curves. Experiments similar to these have been described by Ortner and Stetter,* who also worked with the Greinacher type of linear counter, and further work has been done by Schmidt and Stetter,† who paid particular attention to its use in experiments with H-particles.

Experiments have been made with this apparatus to study the long-range α -particles emitted from radium C and thorium C, and a detailed account of these will be published later. Some of the results for thorium C are given here as a further illustration of the usefulness of this method of counting. The general form of the absorption curve showing the number of these particles exceeding a given range is given in fig. 3. The curve shows two groups of

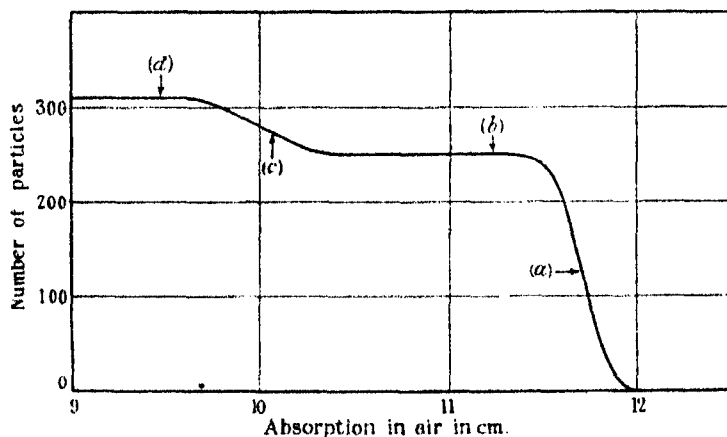


FIG. 3.—Long Range α -Particles from Thorium C.

particles of mean range 11.5 cm. and 9.8 cm. respectively, in good general agreement with the results of Nimmo and Feather,‡ and of Meitner and Freitag§ obtained with the aid of a Wilson chamber. Reproductions of the photographs

* 'Z. Physik,' vol 54, p. 449 (1929).

† 'Z. Physik,' vol. 55, p. 467 (1929).

‡ 'Proc. Roy. Soc.,' A., vol. 122, p. 668 (1929).

§ 'Z. Physik,' vol. 37, p. 481 (1926).

obtained at four different points of the curve are given in figs. 15 (a), (b), (c), (d), Plate 11. The first, fig. 15 (a), corresponding to (a) on the graph (fig. 3), shows kicks of all sizes. This, of course, is a result of the straggling of the α -particles in their passage through matter. Even if expelled with identical velocities, the α -particles travel different distances in the gas, the ranges being distributed in a Gaussian manner about the mean. At a point such as (a) on the curve of fig. 3, some of the particles have not reached the chamber at all, others stop in the middle of it, and others pass right across it, so that a great variety of sizes of kick is to be expected. At (b) all the particles pass right across the chamber, and most of them are on the peaks of their ionisation curves. The second record, fig. 15 (b), was obtained at this point and shows the kicks mainly large but still a little variable in size, as expected. The third record, fig. 15 (c), taken at (c), shows the kicks smaller and more uniform in size. The slope of the ionisation curve for a single particle is small here, so that a given variation in range produces a smaller variation in size than at a point such as (a) or (b) where the curve is steeper. On this record, too, a few very small and very large kicks begin to appear; these correspond to the beginning of the 9.8 cm. range. The last photograph, fig. 15 (d), taken at (d) on the curve, shows large kicks due to the 9.8 cm. particles on the peaks of their ionisation curves, and smaller kicks due to the 11.5 cm. particles. It is exactly analogous to the record (fig. 16) obtained with the main 4.8 and 8.6 cm. particles from thorium C.

From what has just been said it can be seen that, as the source is moved in, a new range can be recognised by the appearance on the record first of a number of small, followed immediately by a number of large kicks. It would, however, be very difficult to recognise in this way a group of particles containing less than 10 per cent. of the main group. Such a small group of α -particles could, of course, be detected by direct counting and plotting the number counted as a function of the absorption, thus obtaining a curve of the type shown in fig. 3. It is not possible, however, to fix its range with great accuracy on account of the probability error involved in counting only a moderate number of particles. Even if at every point of the curve, 1,000 particles were counted, the probable error would be 3 per cent. thus making the uncertainty as much as one third of the total magnitude of the 10 per cent. group under investigation. The differential method next to be described gets over this difficulty, and, under suitable conditions, enables a group of shorter range as small as one thousandth of a main group of α -particles to be detected and its position determined with accuracy.

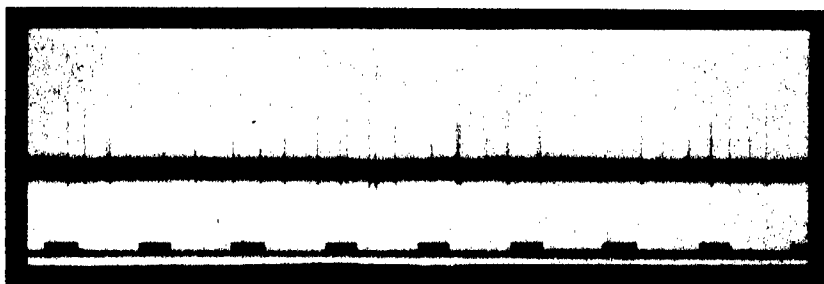


FIG. 15A.—Range beginning to enter—kicks of varying lengths.



FIG. 15B.—Range fully in—kicks of uniform size.

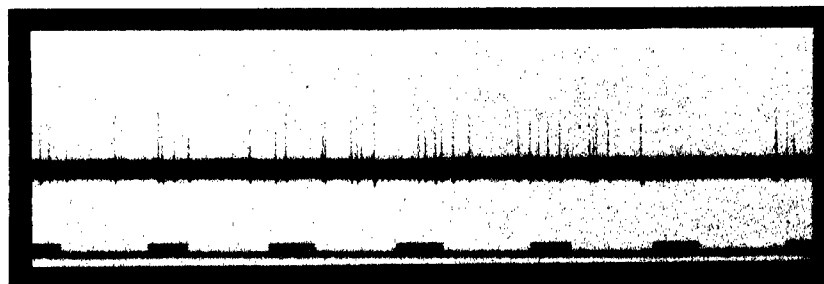


FIG. 15C.—New range entering—shorter and longer kicks recorded.

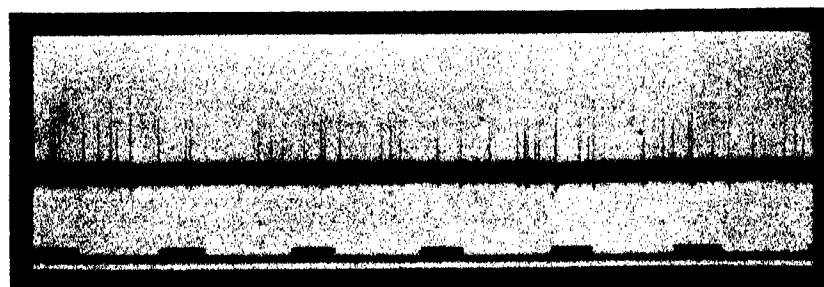


FIG. 15D.—New range fully in—two groups of kicks of different lengths.

(Facing p. 216.)



FIG. 16. --8.6 cm. (short kicks) and 4.8 cm. (long kicks) ranges of Thorium.



FIG. 17A. --Differential chamber--positive chamber alone.



FIG. 17B. --Differential chamber --positive and negative chambers.

The time marks in Figs. 15, 16 and 17 are at one second intervals.

The Differential Method.

The difficulties just described in the investigation of the different groups of α -particles emitted from the same radioactive source could be avoided if it were possible to count, not the total number of particles exceeding a given range, but the number having ranges between, say, x and $x + \delta x$, where δx is of the order of a few millimetres. It is, of course, possible to do this with a Wilson chamber, where the ranges of individual particles are measured, and this method has been employed by various workers to investigate the straggling of single groups of α -particles, and also in experiments on the long-range α -particles from radium C and thorium C. The chief difficulties encountered are scattering from the slits which have to be employed, variations of pressure in the chamber while the α -particles are being photographed, and the danger of small droplets of water condensing on the source or on the slits. Workers with Wilson chambers have always found a number of short tracks associated with a main group of α -particles, and it has never been quite certain whether these were due to scattering or partial absorption of the main group, or were really particles emitted from the source with lower velocity.

We have found it possible, by using a double ionisation chamber with our counter, to record only particles which stop within a range of 1 to 2 mm. of air, and hence to attain most of the advantages of the Wilson-chamber method without its disadvantages for this type of experiment. With this new method particles can be counted at a rate of several hundred per minute, so that the work is much less laborious than with a Wilson chamber.

The Double Ionisation Chamber.

A skelton diagram of the double chamber is given in fig. 4. The first of the two chambers is very similar to the single chamber already described, but the

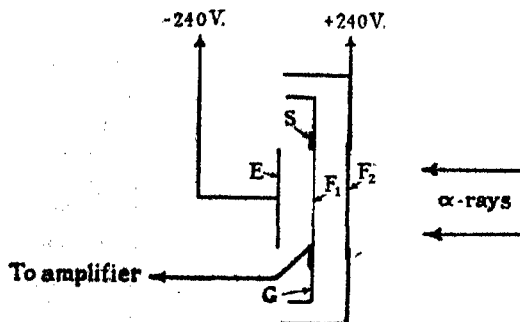


FIG. 4.—Double Chamber Counter.

collecting electrode, instead of being a brass plate, consists of a thin brass ring over which is stretched a thin gold foil, F_1 , of stopping power about 0.4 mm. for α -rays. This also forms the front of the second chamber, which is closed at the back by the brass disc E. Each of the two chambers is 2.5 mm. deep; the front foil, F_2 , is charged to a potential of + 240 volts and the back plate E to - 240 volts. When a particle enters, the positive ions formed in the first chamber and the negative ions formed in the second chamber are driven on to the collecting electrode. If the particle stops in the first chamber or in the foil between the two chambers, the total charge collected will, of course, be positive. If, however, the α -particle is of about 4 mm. greater range than this, the peak of its ionisation curve will lie in the second chamber, and a lower portion of the curve in the first chamber, so that the net charge given to the collecting electrode will be negative. It can easily be shown from the ionisation curve that only particles which stop within a region 6 mm. broad will give a net positive charge.

The curve (fig. 5), shows the charge which is given to the collecting electrode, plotted against the residual range of the particle on entering the first chamber.

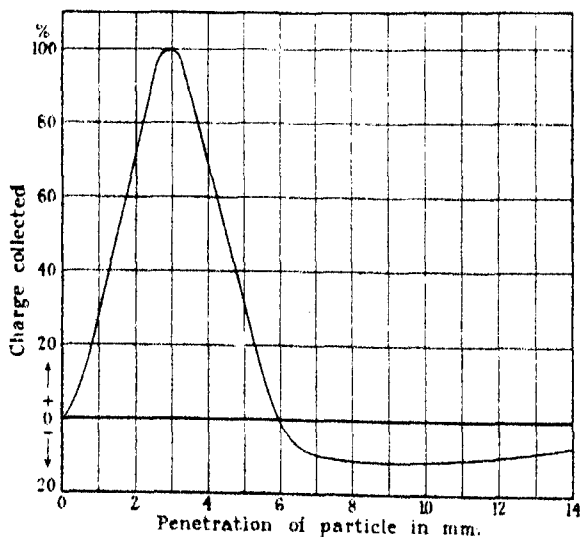


Fig. 5.—Characteristic of Double Chamber.

Positive charges are confined to a region 6 mm. broad, and large positive charges (*i.e.*, over 70 per cent. of the maximum), to a region only 2 mm. broad. If, therefore, on the photographic records given by the oscillograph, only positive kicks of over 70 per cent. of the maximum are counted, these will correspond to α -particles which have stopped within a region 2 mm. broad.

Two examples of photographs taken with the double chamber are shown in figs. 17 (a) and (b), Plate 12. In the first photograph, fig. 17 (a), the back electrode was earthed, so that only the first chamber was in action. Particles are seen to be pouring in at a mean rate of 6,000 per minute. In the second record, fig. 17 (b), both chambers were in action, and it is seen that the number of positive kicks is reduced to 250 per minute, while the very small negative kicks due to the rest of the particles can just be distinguished. This record was obtained with the α -particles of 8.6 cm. range from thorium C'. The positive kicks remaining are due to straggled particles of range about 3 mm. less than the mean.

It is possible to look for short-range particles when as many as 100,000 main particles are passing through the chamber per minute. Rates higher than this cannot at present be employed, as the zero of the photographic record becomes too disturbed. Each of the main particles gives a small negative kick,* and at high speeds of counting these become superposed, and the oscillograph spot is in continual motion.

To reduce this effect as far as possible it is essential to try to prevent superposition by sharpening up the individual kicks. This is attained (a) by making the collection of ions in the chamber as rapid as possible, (b) by introducing a quick back-leak in an appropriate stage of the amplifier, and (c) by employing a high-frequency oscillograph. The oscillograph designed specially for the purpose and employed had a natural frequency of 3,000. As before mentioned, such technical points will be dealt with more fully in a subsequent paper.

Fig. 6 is a detailed diagram showing the design of the double chamber and the source-holder. The front of the first chamber was covered, not with sputtered mica, but with a further thin gold foil, F_2 , in order to reduce as far as possible the amount of absorbing material between source and counter. The counter with these thin foils charged to high potentials close to the free grid system behaved as a condenser-microphone, and the apparatus was exceedingly

* It is of course possible, by adjusting the relative depths of the two chambers, to make the kick exactly zero for a particle of given residual range, and if this were done it might be possible, if desired, to work with the main particles coming through at an even higher rate than 100,000 per minute. But the balance would only hold for one particular point, and, to preserve it, the chambers would have to be readjusted for every point: this would in practice be much too laborious to be worth while. Other arrangements of the relative depths of the chambers and applied potentials could, of course, be used for special purposes. For instance, if the front chamber is made very shallow, say 1 mm. deep and the second one 3 or 4 mm. deep, then all particles stopping in the front chamber will be shown by positive kicks, while the total number of particles passing through will be shown by the large negative kicks.

sensitive to sound-waves. It was quite impossible to work with it out in the open air, and it was found necessary to enclose the whole of the ionisation

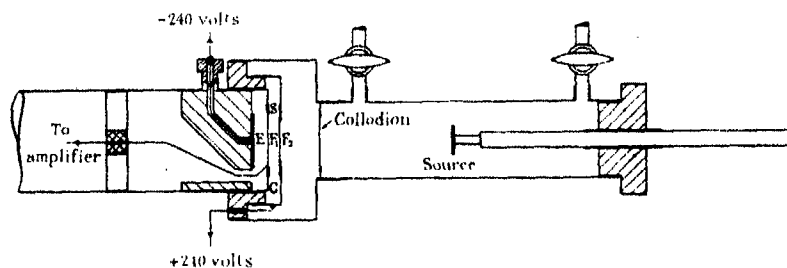


FIG. 6.—Detailed Diagram of Apparatus.

chambers in a gas-tight metal box; all sliding joints had to be waxed up during an experiment, and adjustments of the position of the source were carried out through a ground joint (not shown).

Results Obtained by the Differential Method.

We shall here give four examples of the results obtained by the differential method. The first to be described is a preliminary study of the straggling curves of the 8.6 cm. α -particles of thorium C', the 7.0 cm. particles of radium C' and the 3.9 cm. particles of polonium, all of which are believed to be homogeneous groups of α -particles.

According to the theory of straggling, the ranges in air of such a beam of α -particles should be distributed in a Gaussian manner about a mean. Experiments confirm this distribution, but the distribution coefficient is found in all cases to be greater than that expected from theory. Briggs* has made a careful study of the straggling of the 7 cm. α -particles from radium C', and has found the distribution coefficient, or "straggling coefficient" to be 1.20 mm. for these particles.

Fig. 7 (innermost curve, A) shows the distribution of particles calculated for a straggling coefficient of 0.9 mm., corresponding to α -rays of range between 4 and 5 centimeters. The experimental distribution to be expected for the differential counter will be slightly broader than this, for the counter records the number of particles which stop, not within an infinitesimally small interval dx , but within a region about 2 mm. broad. The actual "effective breadth of slit" (i.e.,—effective depth of chamber) depends on the size limit over which particles are counted, as previously explained. The middle and

* 'Proc. Roy. Soc.' A., vol. 114, p. 313 (1927).

outer curves (B and C) of fig. 7 show the effect of viewing the innermost curve through slits 2 mm. and 3 mm. broad respectively. The most convenient way

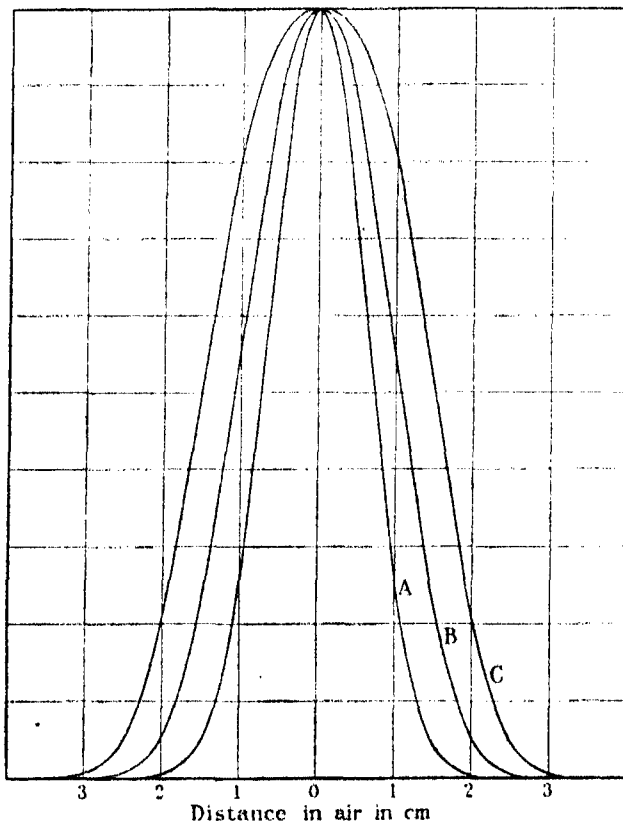


FIG. 7.—Theoretical Distribution Curves for Polonium α -particles.

A, True Straggling Curve. B, Observed Curve, 2 mm. Slit. C, Observed Curve, 3 mm. Slit.

of measuring the "breadth" of such a curve is to draw tangents through the approximately straight side portions and to measure the intercept between these tangents on the x -axis. For a true straggling curve, this intercept should be $2\sqrt{2}$ times the straggling coefficient.

Fig. 8 (a) shows the experimental curve for polonium, obtained with the differential counter. It is seen that the curve is very nearly symmetrical, but that there is a small "tail" on the low-velocity side. All evidence so far available tends to show that this tail is due, not to initial inhomogeneity of velocity, but to scattering or absorption. Unless the source is prepared with extreme care, a much larger tail than this is obtained. We hope shortly to make a fuller investigation on this point.

Fig. 8 (b) shows the experimental curve for radium C', obtained with a very clean source which had been prepared in a way to be described later in this

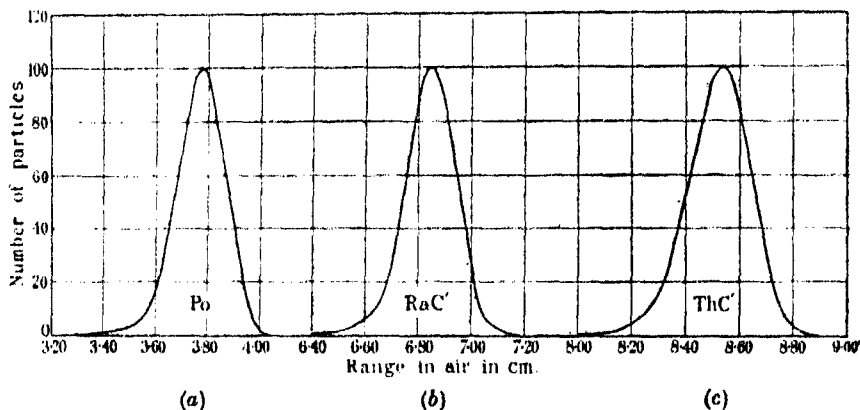


FIG. 8.—Experimental Curves for Polonium, Radium C' and Thorium C'.

paper. It will be noticed that the curve is almost exactly the same width as the polonium curve. The reason for this is that, in obtaining it, particles were counted between rather narrow size limits, so that the effective slit width was only 0.7 mm. The "tail" is similar to the one found for polonium. It has been carefully investigated from 7 cm. right back to 3 cm. absorption, at which point its magnitude was 1 in 7,000 of that of the main peak, while at 6 cm. it was 1 in 1,000. These values are much smaller than those previously found with expansion chambers. The main peak of radium C' appears accordingly to be homogenous to a high degree.

Very similar results have been found for the 8.6 cm. group of thorium C', as shown by fig. 8 (c), and this also appears to be a homogeneous group. The results obtained with the 4.8 cm. α -rays from thorium C and the 5.5 cm. rays from actinium are, however, markedly different, as described below.

Analysis of the α -Rays from Actinium C.

In our experiments, the active deposit of actinium, consisting of actinium (B + C), was obtained by exposing a negatively-charged brass disc in the presence of the emanation from a preparation of actinium in equilibrium. Some time after removal it is well known that the α -ray activity decays exponentially with a half-value period of 36.1 minutes. A source of convenient strength was carefully prepared, and the α -rays were examined by the differential method. The results obtained are shown in fig. 9. It is seen that not one, but two well-marked maxima are present, corresponding to two groups

of α -particles differing in range by 4.2 mm. The observed straggling curves of these two groups, which are completed by the broken lines, are of the breadth to be expected for two homogeneous groups of range about 5.5 and 5.1 cm. Geiger* found the extrapolated range of the α -rays from actinium C to be 5.51 cm. at 760 mm. and 15° C. Assuming that this is the correct value for the range of the stronger group, the extrapolated range for the weaker group is 5.09 cm. From the corrected v^3 law, the individual energies of the α -particles in these groups are 6.61×10^6 and 6.27×10^6 electron-volts respectively. It was found that the intensity of the two groups decayed with the same

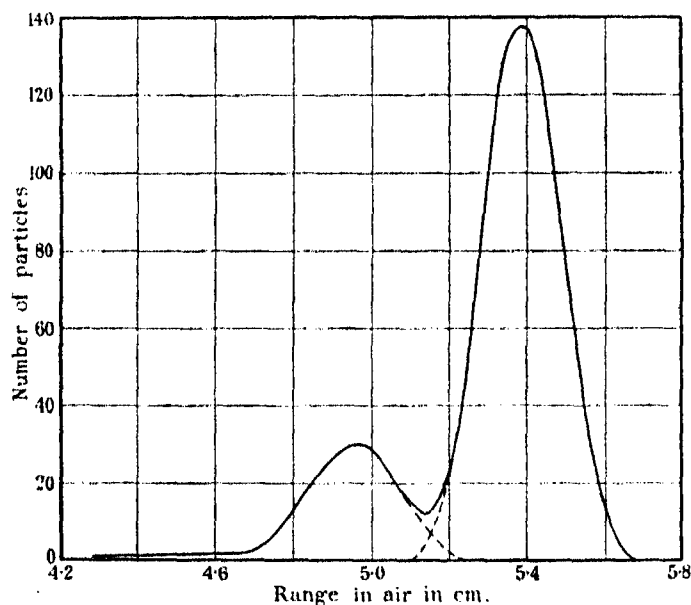


FIG. 9.—Experimental Curve and Analysis of α -Particles from Actinium C.

period, reaching half-value in 36 minutes. Taking the number of α -particles in the main group as 100, the number in the second group is 22.

These results indicate that, like the other "C" bodies, actinium C gives a complex α -ray emission. We have made preliminary observations on the weak group of long-range α -particles of range about 6.5 cm., first noticed by Marsden and Perkins† in 1914, and found by them to be present to an extent of about 0.3 per cent. of the main group; the detailed analysis of this group will be considered in a later paper. It is of interest to note that it was long ago suggested that the main α -rays from actinium C were complex. Mlle.

* 'Z. Physik,' vol. 8, p. 45 (1921).

† 'Phil. Mag.,' vol. 27, p. 690 (1914).

Blanquies* in 1909 compared the Bragg ionisation curves for a pencil of α -rays from polonium, radium C and actinium C. When the maxima of the Bragg curves were made to coincide, the ionisation curves for the α -rays from polonium and for radium C were found to be very nearly the same, but the peak of the curve for the α -rays from actinium C was markedly broader. The question was re-examined in 1914 by Marsden and Perkins. They observed that the sharpness of the curve near the maximum depended on the range of the α -rays, as is to be expected from our knowledge of the straggling of α -particles. The shape of the curve near the maximum for α -rays from thorium C' (range 8.6 cms.) was markedly broader than for the α -rays from polonium (range 3.9 cms.), while the ionisation curve for the α -rays from actinium C (range 5.5 cms.), was intermediate, being nearly the same as for the α -rays from radium C (range 7.0 cms.). The conclusions of Marsden and Perkins on these data were indefinite. If the α -rays of actinium C were complex, the effect appeared to be much less marked than that noted by Blanquies.

If, as we have shown, the α -rays from actinium C consist of two groups of range 5.51 cms. and 5.09 cms. in the ratio of 22 : 100, it is easy to deduce that the Bragg ionisation curve should be much broader near the maximum than is to be expected for a group of homogeneous α -rays of range 5.51 cms. It is to be expected that if a narrow beam of α -rays and a shallow ionisation chamber were used, the ionisation curve would show two maxima, separated by a shallow dip. If the curve were obtained in hydrogen instead of in air, so as to reduce the effect of straggling, the two maxima should be easily observed.

The α -Rays from Radium C.

It is generally agreed that the atoms of radium C break up in two distinct ways, illustrated in the diagram (fig. 10), where the radiation and atomic number

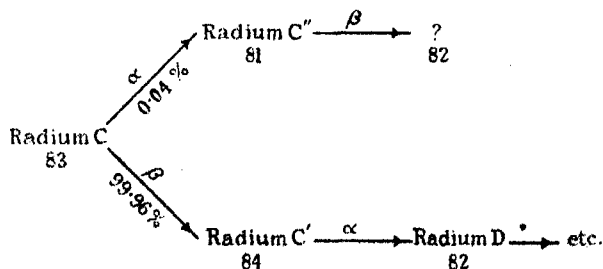


FIG. 10.—Dual Disintegration of Radium C.

* 'Le Radium,' vol. 6, p. 230 (1909), and vol. 7, p. 159 (1910).

of each product are added. About 0.04 per cent. of the atoms break up with the emission of an α -particle and give rise to the β -ray product, radium C'', which is half transformed in 1.38 minutes. The reverse process is assumed to take place in the other branch. Radium C', which emits a swift α -particle (range 7.0 cms. in air) has a very short period of transformation, estimated by Jacobsen* to be about 10^{-6} second.

The product radium C'' was first obtained by Hahn and Meitner† by recoil from a nickel plate coated with radium C. It was investigated in detail by Fajans,‡ who concluded that it must arise from an α -ray recoil from radium C. By comparison of the β -ray activity of radium C'' with that of radium C, he concluded that about 1 in 3,000 of the atoms of radium C were transformed into radium C''. This ratio has been measured in a similar way by Albrecht,§ who found its value to be 1 in 4,000. From the transformation theory and the Geiger-Nuttall relation, it can be deduced that the range of the α -rays from radium C should be about 3.9 cms. in air.

It is seen that the emission of α -rays from radium C has been inferred from the vigour of the recoil which leads to the separation of radium C''. All attempts to detect this weak group of α -rays (1 in 3,000) in the presence of the strong group of α -rays of range 7 cms. have ended in failure. A few years ago Rutherford made a number of experiments on this point. An intense beam of α -rays from radium C was bent by a strong magnetic field, and the number of scintillations on a zinc sulphide screen were counted, well outside the main deflected beam. Although care was taken in the preparation of the source, the continuous distribution of α -particles due to the scattering by the source and slit and other causes was found to be too marked to allow the presence of such a weak homogeneous group of α -rays to be detected.

Further experiments by a similar method were made last year by Mr. C. A. Lea, in the Cavendish Laboratory. Special care was taken in the preparation of the source and in the arrangement of the slits to reduce the scattering as far as possible, but again it was not found possible to reduce the continuous background of α -particles sufficiently to allow the detection of the missing group.

Since by the new methods the constitution of a beam of α -rays can be analysed without the use of narrow defining slits, it was hoped that the inhomogeneity

* 'Nature,' vol. 120, p. 874 (1927), and 'Phil. Mag.,' vol. 47, p. 23 (1924).

† 'Phys. Z.,' vol. 10, p. 697 (1909).

‡ 'Phys. Z.,' vol. 12, p. 369 (1911).

§ 'Wien. Akad. Ber.,' vol. 128, p. 925 (1919).

produced in a beam of α -rays by scattering would be sufficiently reduced to enable the missing group to be detected. The general arrangement of the experiment was similar to that already described. The defining diaphragm was 8 mm. in diameter. Special care was taken to obtain a source of α -rays from radium C as homogeneous as possible, and for this purpose the recoil method of collection was used. A strong source of radium A was obtained on a metal plate, and the recoil atoms of radium B were collected on a negatively charged plate in air in the usual way. In the centre of the collecting plate was an aperture 5 mm. in diameter, over which was placed a polished brass disc 8 mm. in diameter, which was to serve as the source of α -rays. In this way a deposit of radium B, and, ultimately, of radium C, was obtained, of convenient strength. The active material was distributed only in the central portion of the disc, and edge effects were completely avoided.

The variation with time of the α -ray activity of such a source is well known. For a short time of collection of radium B, the activity due to radium C passes through a maximum after an interval of about 40 minutes, and ultimately decays with the period of radium B, falling to half value in 26 minutes. Tables for the variation of activity with time have been given by Meyer and Schweidler.* The number of α -particles emitted by the source per minute was determined at the maximum by direct counting with the single chamber, using a defining diaphragm of diameter 1 mm. The activity at any subsequent time was calculated from the known decay curve, and verified by direct counting at the end of the experiment.

Since the number of α -particles to be expected from the radium C'' group was 1 in 3,000 of the main number, it was essential for rapid counting that a large number of α -particles from the main group should enter the analysing chamber per minute. In practice, the source strength was so chosen that from 30,000 to 60,000 α -particles entered the chamber per minute. Even under these conditions, the number of α -particles to be expected from the radium C'' group for an absorption corresponding to its mean range should be between 10 and 20 per minute. For reasons previously discussed, it was not practicable to allow the main particles to pass through at a rate much greater than this.

With the precautions taken to reduce scattering to a minimum, the background was sufficiently reduced to allow a reasonable chance of finding the short range group of particles. The results obtained are shown in fig. 11. The curve shows, as expected, a continuous background upon which is super-

* "Radioaktivität," 2nd edition, p. 434.

imposed a definite peak. The curve was obtained by combining the results of four separate experiments, in which a total of 4,000 α -particles were counted.

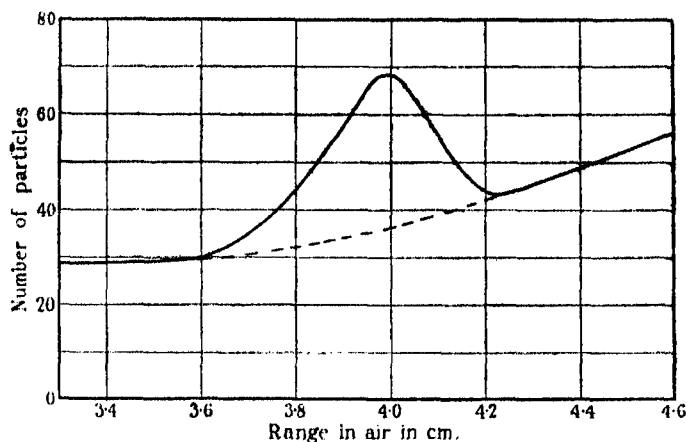


FIG. 11.—Experimental Curve for Radium C α -particles.

Each separate experiment showed the essential characteristics of the curve. Both the peak and the background were found to decay with the same period as the main 7 cm. α -particles group from radium C'.

The broken line in fig. 11 shows a continuation of the background, while the difference between the actual and the broken curve is plotted in fig. 12. This

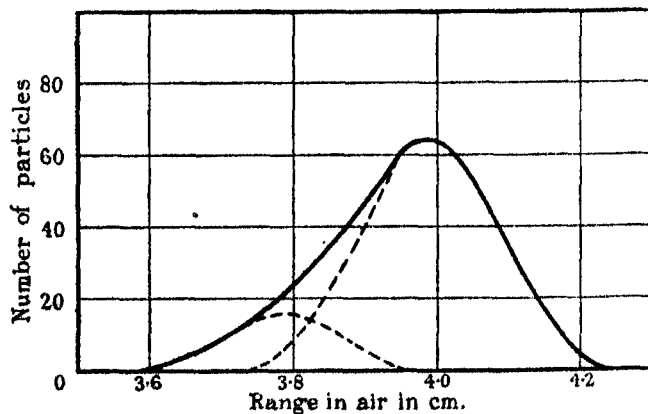


FIG. 12.—Analysis of α -particles from Radium C.

curve shows what the group of particles would be like if the background could be entirely removed. By comparison with the curve for polonium, it is seen that the width of the curve is greater than that for a single group of α -particles of range 4 cm. Further, the radium C curve is definitely unsymmetrical. This

asymmetry appeared in every individual experiment, and there is little doubt that it is real. We have already seen that the α -rays from actinium C are complex, consisting of two groups differing in range by 4.2 mm., and it will be seen later that Rosenblum* has shown that the α -rays from thorium C are still more complex, consisting of several groups. It is accordingly not unexpected that the α -rays from radium C will also be complex.

The experimental curve we have obtained (fig. 12) can be analysed as shown by the broken lines to show two component ranges, of relative intensities 3 : 1, separated by 2.0 mm. We do not wish to lay too much stress on the accuracy of the range or the relative intensity of the weaker component. It is difficult in experiments of this kind to determine with accuracy the exact shape of the curve, against the uncertain background. Only a moderate number of α -particles—usually about 100 to 150—could be counted at each point of the curve, and the probable error in this number is nearly 10 per cent. If the background could be reduced to, say, one-third of its present value, the accuracy with which the curve could be determined would be greatly increased.

The ranges were found to be 2.2 mm. and 0.3 mm. respectively greater than the polonium range. Assuming the extrapolated range of polonium to be 3.925 cm. (Geiger) at 15° C. and 760 mm., the extrapolated ranges of the two groups (calculated at 15° C. and 760 mm.) are 4.14₅ cm. and 3.95₅ cm., corresponding to energies of 5.45×10^6 and 5.28×10^6 electron volts respectively; their relative intensities are 3 : 1, while the stronger component is 1 in 5,000 of the main 7 cm. group of α -particles from radium C''. The two groups together thus amount to just over 1 in 4,000 of the main group, in very good agreement with the value deduced from the intensity of the β -rays from radium C'' by Fajans and Albrecht.†

The continuous spectrum has been investigated over the whole region from 2.5 cm. up to the main 7 cm. particles; it was not possible with the present apparatus to get closer to the source than 2.5 cm. No evidence was found of any other peak. The intensity of the background varied with the range in a way to be expected if it is due to scattering or partial absorption of the main beam of α -rays; at 5.9 cm. it was 0.1 per cent., at 4.5 cm. 0.025 per cent., and at 3.0 cm. 0.015 per cent. We have not so far examined whether the background can be reduced by variation of the material of the source, the nature of the gas, or the arrangement or material of the defining diaphragm, but we hope to investigate this later. Both aluminium and brass sources were

* 'C. R.', vol. 188, p. 1401 (1929), and vol. 190, p. 19 (1930).

† *Loc. cit.*

tried, but no certain difference could be detected between them. It is important to decide whether the background can be entirely explained by scattering in the source, the gas and diaphragms, and absorption in passing through the gas. There is at present no experimental evidence of the relative importance of these factors.

Analysis of the α -Rays from Thorium C.

In order to examine the fine structure of the α -rays, Rosenblum* has employed the focussing method so much used in the examination of β -ray spectra. For this purpose the large electromagnet of the Academy of Sciences, constructed by Cotton, was used, and in the later experiments, the α -rays were bent in a semi-circle of diameter about 35 cm., using a field of about 23,000 gauss. By this method, beautiful photographs have been obtained showing the fine structure of the α -rays from thorium C (range in air 4.8 cm.). The results obtained are shown in the following table, where the velocity of the strongest line is taken as unity and its intensity as 100.

Designation of line.	Velocity.	Relative intensity.
α	1.0000	100
α_1	1.0034	30
α_2	0.9758	3
α_3	0.9624	2
α_4	0.9640	0.5

The difference in range in air between α and α_1 should be only about 0.5 mm. ; the difference between α and α_2 is 3.5 mm., and between α and the mean range of α_3 and α_4 about 5.2 mm. While it is of course evident that the method of magnetic analysis used by Rosenblum gives much greater resolution than our counting methods, it is of interest to see whether the presence of the lower velocity groups found by him can be detected by the differential analyser. The difference in range between the groups α and α_1 —viz., 0.5 mm.—is too small to hope to resolve by our method, but we should be able to obtain evidence of the groups differing in range by 3.5 and 5.2 mm. from α .

The actual experimental curve obtained with thorium C α -rays is shown in fig. 13 (curve A). It is seen that there is a subsidiary peak on the low velocity side of the main peak (only a portion of which can be shown in the figure). It is a little difficult to determine with accuracy the form of this subsidiary peak, as the shape of the "tail" of the main peak (corresponding to lined) is not

* *Loc. cit.*

known, and further, its position depends on the "effective width of slit" employed. After careful consideration of the shape and position of the tails experimentally found for thorium C' (of 8.6 cm. range), radium C' (7.0 cm.)

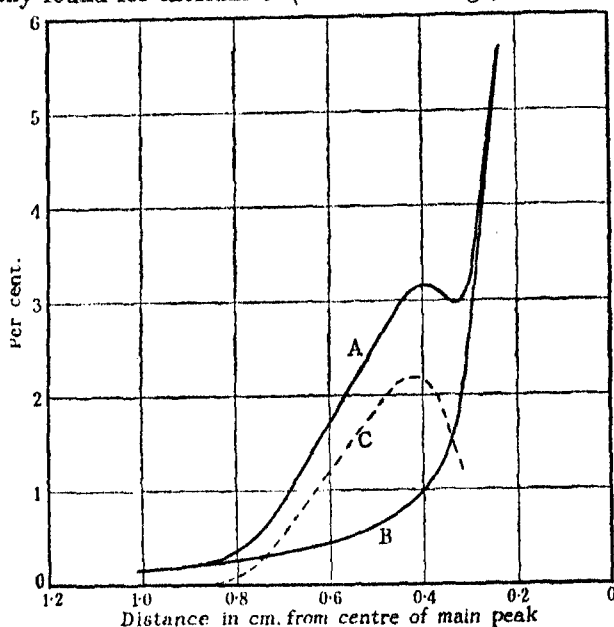


FIG. 13.—Experimental Curve and Analysis of α -Particles from Thorium C.

and polonium (3.9 cm.), the lower full curve (B) of the figure has been drawn to show the most probable form of the tail to be expected from thorium C under the conditions of the experiment. The portion of the curve between 0.80 cm. and 0.35 cm. is probably fairly accurate, but to the right of this it is very uncertain. The broken curve (C) shows the difference between the experimental curve and this tail, and should give a representation of the effect of the three ranges α_2 , α_3 and α_4 . Fig. 14 shows the curve to be expected from

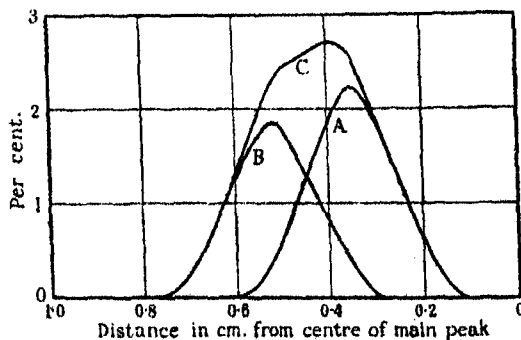


FIG. 14.—Curve for Thorium C α -particles, reconstructed from Rosenblum's Data.

Rosenblum's data and the known form of the straggling curve for a homogeneous group of α -particles; the two component curves (A and B) due to α_2 and $(\alpha_3 + \alpha_4)$ respectively, and their sum (C) are shown in the figure.

Considering the uncertainty of the experimental curve, due to the uncertainty as to the form of the "tail" to be expected, the agreement between the two curves may be considered satisfactory. The positions of the maxima of the two curves agree to within 0.2 of a millimetre, and their heights are in fair accord, our experimental height being about three-quarters of the height deduced from Rosenblum's data.

Discussion.

The results we have just described show the usefulness of the new methods—especially of the differential method—in investigating the complexity of α -ray groups. The early experiments with α -rays seemed to show that, in sharp contrast with the β - and γ -ray spectra, α -ray spectra were exceedingly simple; in fact, it appeared that each α -ray body emitted only α -rays of one definite velocity. The first departure from this simplicity came with the discovery of the long-range α -particles from thorium C by Rutherford and Wood* in 1916. In 1919 Rutherford† showed that long-range particles were also found with radium C sources, and proof was later obtained that these were true α -particles emitted from the source. Further experiments by various workers have shown that the long-range α -particles do not form one homogeneous group, but are themselves complex. Recently, as described above, Rosenblum has shown that the "normal" α -particles of range 4.8 cm. from thorium C are also complex, consisting of at least five groups of particles.

From the observation that the α -particles from a radioactive element all appear to be expelled with identical velocity, it has generally been supposed that the emission of an α -particle is dependent on quantum conditions in the nucleus. It was natural to suppose that the α -particle before emission occupied the same energy level in all the nuclei. It is now evident that the simple model of the nucleus is not adequate. It appears that in the nuclei of radium C and C' and of thorium C and C' there must be a number of possible α -ray levels, some higher and some lower than the normal levels. It is simplest to suppose that among all the nuclei to be transformed there is a certain probability that the α -particle at the moment of its emission may be found in each of a number

* 'Phil. Mag.' vol. 31, p. 379 (1916).

† 'Phil. Mag.' vol. 37, p. 571 (1919).

of possible levels. Since it is of great importance to determine all possible α -ray levels in the radioactive nuclei, it is obviously desirable to obtain as much evidence as possible on the simplicity or complexity of the α -rays from various radioactive bodies.

Our results so far obtained with the differential counter can only be considered as preliminary. As far as we can at present ascertain, the α -rays from polonium, radium C', and thorium C' appear to be entirely homogeneous,* in accordance with Rosenblum's results for these bodies.

We have been able to verify the existence of the weak "companion lines" of thorium C as found by Rosenblum, though of course his results, obtained by the magnetic deflection method, show the fine structure in much greater detail than we could hope to attain. We have shown that, as previously suspected but not proved, the main α -rays from actinium C show two distinct groups, and further, that the missing α -rays from radium C, which we were able to find, also appear to be complex. In this case, on account of the experimental difficulties involved in detecting such a weak group, we are not able to give precise data on the fine structure of the group, though the position and intensity of its maximum can be given with fair certainty.

It is probably significant that these bodies, radium C, thorium C and actinium C, which give complex α -rays, are all of odd atomic number, whereas all the other known α -ray bodies, with the exception of protoactinium, are of even atomic number. It will be of great interest, for this reason, to look for complexity in the α -rays from protoactinium, and we hope to do this shortly. On general grounds it is not unlikely that the system of levels in the nucleus of an odd-numbered element may be quite different from those of an even-numbered element.

It will be seen that the study of the α -ray groups from various radioactive bodies opens out an interesting field of work, on which at present little definite information is available. For this purpose, both Rosenblum's method of magnetic deflection and focussing and the differential counting method should prove of great service in their respective spheres. Rosenblum's method is ideally much the better, for besides having far greater resolving power than ours, it gives directly the velocities of the α -particles under investigation. Our method, however, has certain practical advantages which make it valuable as

* Neither of these sets of results, of course, precludes the existence of very weak groups, of intensity of the order of a thousandth of that of the main group and close to it. If with our counter, the background due to scattering can be still further reduced, it will be possible to search more carefully for such groups.

an additional method of experiment. Results can be obtained easily and quickly, and, further, it can be used with very weak sources. This fact should make it valuable for studying the α -rays from feebly radioactive bodies, where only weak sources are available. On account of the large area of the counting chamber, comparatively weak sources of α -radiation like the long-range α -particles from radium C and thorium C can be analysed in detail. The wide defining diaphragm employed reduces the effect of scattering by slits to a minimum, and this makes possible under some conditions the detection of groups of α -rays of very weak intensity in the presence of the main group of particles. It will be of interest to see whether it is possible by the magnetic method to detect the weak group of α -rays from radium C, which has been readily observed and defined by the counting method.

By measurement of the position of the straggling "peaks" found with the differential counter, it is simple to determine the mean range of a group of α -particles with accuracy. As far as our observations have gone, it should be possible in this way to determine the relative ranges of homogeneous groups of α -rays with an accuracy of 1 in 500 or even better. It is intended to apply the method to a redetermination of the ranges of α -rays from products where only weak sources are available.

Summary.

The paper describes some of the applications of the "Greinacher" type of counter for α -rays, in which the ionisation current due to a particle is amplified linearly by means of thermionic valves, there being no ionisation by collision. It is shown that this counter is valuable in studying complex beams, such as the long-range α -particles from radium C and thorium C.

By using a double ionisation chamber with this type of counter it is possible, when working with complex beams of α -particles, to record only those particles which stop within the chamber itself, and not those which pass right across it, thus giving a measure of the number of particles having ranges between, say, (x) mm., and $(x + 2)$ mm. This differential counter has been applied to the study of groups of α -particles emitted from various sources. The 8.6 cm. α -particles from thorium C', the 7.0 cm. particles from radium C', and the 3.9 cm. particles from polonium all appeared to be homogeneous groups. The 5.5 cm. particles from actinium C, however, were found to consist of two well-marked groups, differing in range by 4.2 mm. The 4.8 cm. particles from thorium C were also found to be a complex group, in agreement with the results of Rosenblum, obtained by the magnetic deflection method.

With the differential counter, the missing short-range α -particles emitted in the dual disintegration of radium C have been found and their constants determined. These particles correspond to the transformation of radium C into radium C'', which was first obtained by Hahn and Meitner by recoil. It is found that these α -particles are present to an extent of about 1 in 4,000 of the main 7.0 cm. particles from radium C'; they appear to consist of two groups—the main one of range 4.1 cm., and a smaller one of range 3.9 cm.

We wish to express our thanks to Mr. G. R. Crowe, who prepared the radioactive sources and assisted us in the experiments.

The Sorption of Carbon Tetrachloride at Low Pressures by Activated Charcoals. Part II.—Isothermals at 25° C.

By A. J. ALLMAND, F.R.S., and R. CHAPLIN.

(Received May 26, 1930.)

The experimental methods employed in this work were described in Part I,* and nothing will be added beyond reference to special points of importance in the particular experiments concerned. As the data obtained have no absolute significance, diagrams will be usually employed to the exclusion of tables of results. This method has the additional advantage of making the relations observed more immediately obvious. The data will, in general, be plotted in the form of the logarithm of the carbon tetrachloride charge (milligram per gram charcoal) against the logarithm of the carbon tetrachloride pressure (millimetre of mercury).

(1) *Directly Determined Isothermals.*

The experiments will be described in the order in which they were done with a view to making more clear the reasons for the modifications in experimental procedure adopted as the work proceeded.

Experiment 1.—A specimen of charcoal C, degassed at 110° C., was employed. It was charged up at 25° C. to 82.3 mg./gram and the pressure measured. After the next point had been determined (160.8 mg./gram), the charcoal was charged up to an estimated figure of 260 mg./gram, and then desorbed for 20–30 minutes whilst being warmed up by immersing the charcoal tube in hot water. Following on this the third point (236.3 mg./gram) was determined. The charcoal was then desorbed by stages down to 50.4 mg./gram (point 10), and there successively followed two sorption points, two desorption points and a sorption point (No. 15). Finally, the charcoal was again heavily charged with carbon tetrachloride (estimated value at least 250 mg./gram) and the final pressure reading (point 16) taken. When obtaining desorption points, the charcoal was in every case first pumped down at 25° after reattachment of the charcoal tube to the apparatus, and then desorbed at a raised temperature, pumping continually and keeping the clean-up charcoal at liquid air temperature. For this purpose the charcoal tube was usually immersed in hot water at 90°–95°. In obtaining point 10, the tube was heated to 100°–105° for

* Chaplin, 'Proc. Roy. Soc.,' A, vol. 121, p. 344 (1928).

5 hours in an electric furnace, and it was the slow rate of loss of carbon tetrachloride that made us decide that the next point should be a sorption point.

The experimental figures are plotted in fig. 1 (crosses and broken curve). Points 1 and 2 are seen to fall right off and above the main curve, whilst there appears to be an abrupt change in direction between points 7 and 8, points 8-11

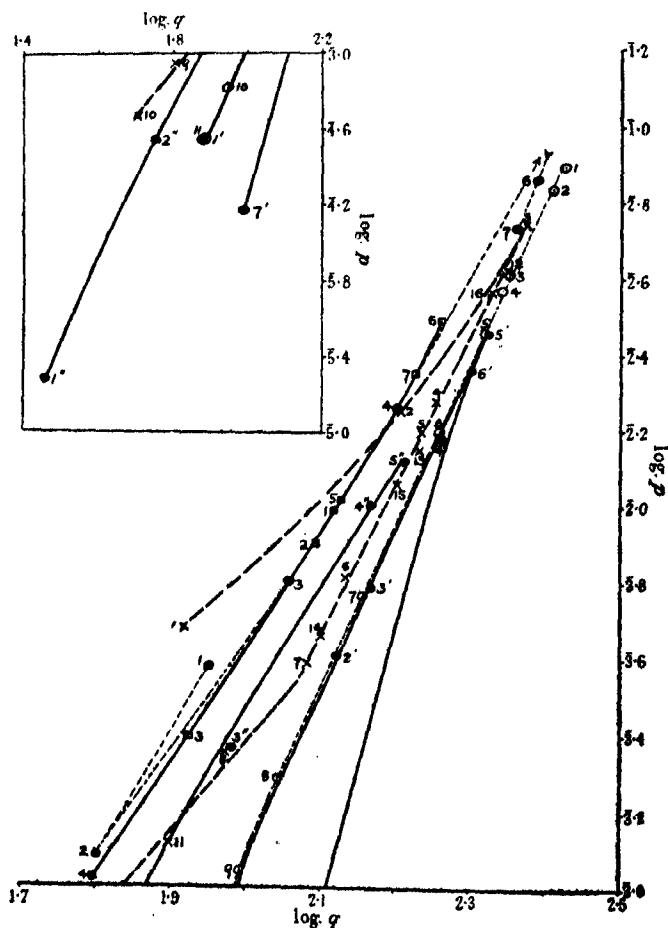


FIG. 1.

(q values all below 100 mg./gram) lying at higher pressures than would be expected from the majority of the figures. These (3-7 and 12-16) all fall moderately well on a straight line.

This experiment was not regarded as particularly satisfactory. The technique had not, at that stage, been worked out fully. The best method of exactly

defining the gauge zero was in doubt and, more particularly, the method afterwards developed for the estimation of gaseous impurities present in the carbon tetrachloride vapour was not in use. But that such impurities (the presence of which was judged likely from the work of Harned*) were probably fed into the vapour from the charcoal during the experiment was shown by the fact that if, after an apparent equilibrium pressure had been measured, the vapour present in the gas space were pumped off and equilibrium then allowed to re-establish itself by evolution of carbon tetrachloride from the charcoal, the new pressure (i.e., the voltage reading of the Pirani gauge) was sometimes found to be appreciably less than the former one, although the amount of carbon tetrachloride removed from the apparatus was quite negligible. The first sorption points showed this phenomenon much more markedly than the later desorption and resorption points, and the procedure mentioned had to be repeated several times before constant pressure readings were obtained. (Naturally all pressure readings plotted by us are these final "constant" readings.) It was concluded that the assumed presence of this gas displaced from the charcoal by the sorbate in some way or another was responsible for the high pressure readings obtained with points 1 and 2, and that if this displacement could be effected beforehand, and the gas removed from the apparatus a reversible curve might at once be expected.

Experiment 2.—Charcoal C, degassed under the same conditions, was again used, but this time charged up initially to about 160 mg./gram, and then desorbed down to 131.4 mg./gram before taking the first pressure reading. There was no sign of any drop in pressure, such as mentioned above, on taking charges of vapour out of the apparatus. Three more desorption points were taken, followed by two sorption points and a final desorption point (No. 7). The data are plotted in fig. 1 (squares and continuous curve). The points fall on a curve very slightly convex to the $\log q$ axis, there is no hysteresis, and the isothermal is a reversible one. It will be noted that the pressures are throughout higher than those of experiment 1, excluding the initial sorption point.

The procedure of experiment 2 having thus resulted in a reversible isothermal, two other charcoals were investigated in a similar fashion.

Experiment 3.—Charcoal A was evacuated at 110° C., charged to about 135 mg./gram, and desorbed down to 45.0 mg./gram, at which the first pressure reading was taken. Four resorption points were measured, then three desorption points and a final resorption point (No. 9). The results are plotted

* 'J. Amer. Chem. Soc.,' vol. 42, p. 372 (1920).

in fig. 2 (squares and continuous curve) and, with one or two exceptions, lie on a satisfactory straight line.

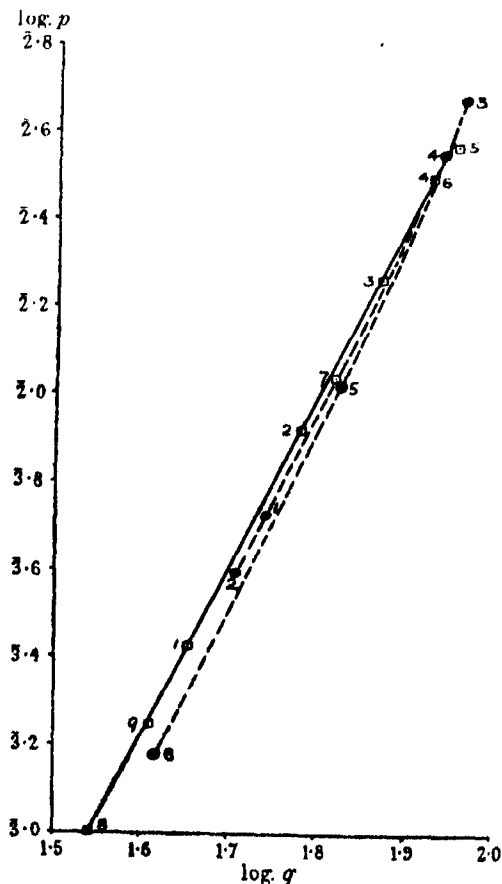


FIG. 2.

Experiment 4.—Charcoal B was evacuated at 110°C. , charged to about 100 mg./gram, and desorbed down to 19.0 mg./gram, at which the first pressure reading was taken. Five resorption points were measured, then four desorption points and a final resorption point (No. 11). The results are plotted in fig. 3 (squares and continuous curve). Point 10 falls right off the curve. This is very probably due to experimental error, as the pressure measured was of the order of 10^{-4} mm., and the sensitivity of the gauge voltmeter then in use (2.5×10^{-4} mm.) was insufficient for the purpose. The remainder of the results fit fairly well on a linear curve, but not as accurately as do those of

experiment 3. It may be noted that point 7 was obtained by desorbing at 25° C. from point 6 and not, as usual, by desorbing at 90°–95°, and that point

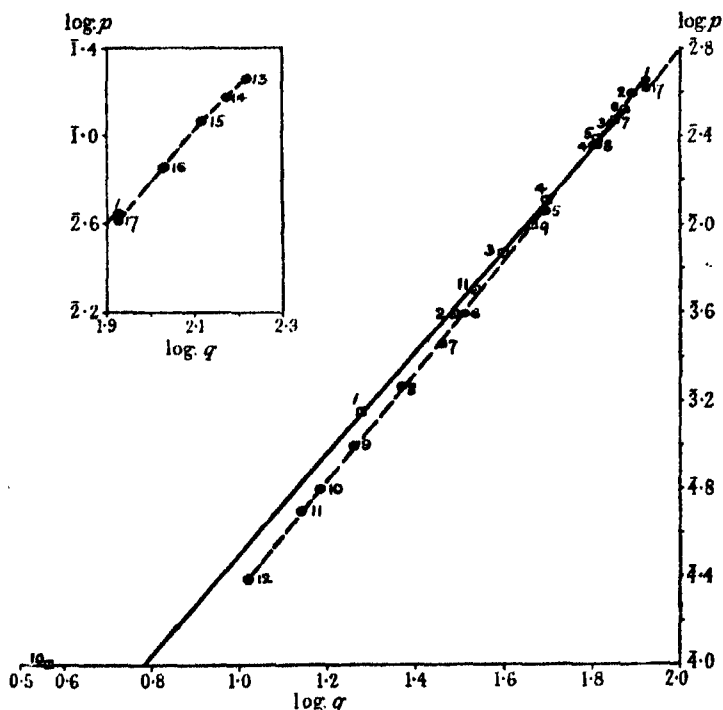


FIG. 3.

11 was determined after the charcoal had been standing for 3 weeks at room temperature with the low carbon tetrachloride charge of point 10.

One disadvantage about the initial procedure adopted in experiments 2–4 is that it makes the determination of points at low q values a tedious process, the desorption of a charged charcoal becoming naturally very slow as the carbon tetrachloride pressure above it falls (*cf.* experiment 1). It was therefore decided to attempt once again to obtain a reversible isothermal in which the low quantity points were first measured, introducing successive small quantities of carbon tetrachloride to the freshly evacuated charcoal, but at the same time heating up and pumping off any displaced gases *during the sorption process*. In this way it was hoped that the complication ascribed to the presence of such gases would be overcome.

Experiment 5.—A specimen of charcoal D, evacuated at 110° C., was charged up to 13.8 mg./gram, using the procedure just indicated, and its pressure

measured. Six further sorption points were then determined, the maximum q value reached being 105.2 mg./gram. These were followed by seven desorption points (point 14 = 45.7 mg./gram), by four resorption points and two final desorption points (19 and 20). The results are plotted in fig. 4

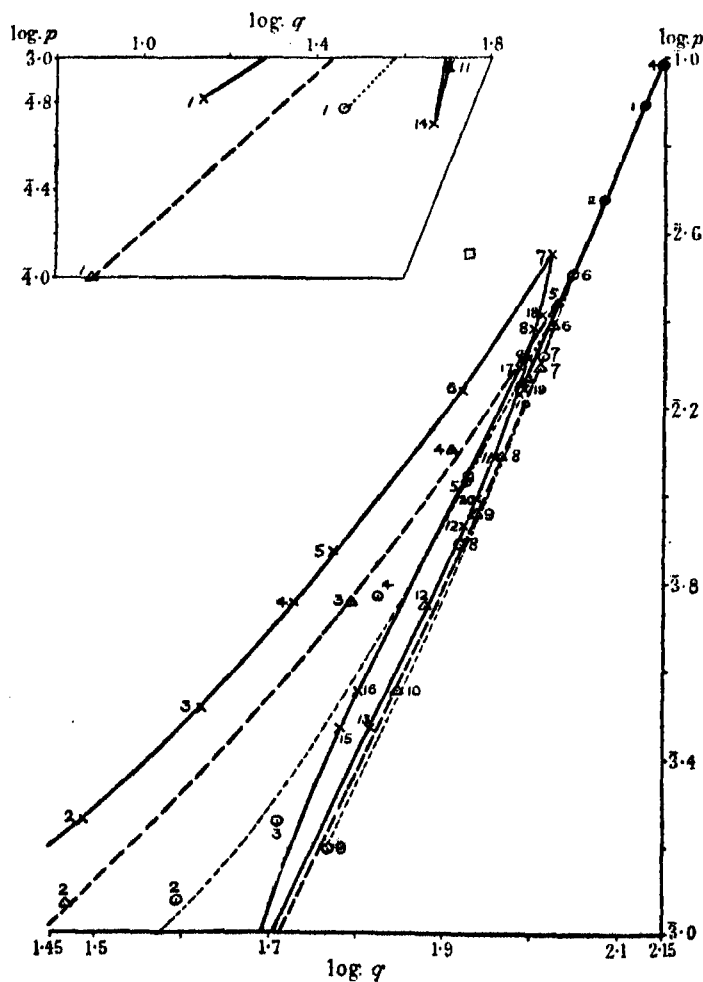


FIG. 4.

(crosses and continuous curve) and are of considerable interest. Contrary to our anticipation, the isothermal shows marked hysteresis and irreversibility. In spite of heating the charcoal up when charging for the initial low quantity sorption points, the relative positions of these points with respect to the first set of desorption points, is much as was found in experiment 1, where the

initial charging was done at 25° C. Moreover, the resorption points 15 and 16 also show hysteresis, in the sense that their pressures lie above those of the preceding desorption points. In this respect the behaviour of charcoal D resembles that shown by various charcoals (including D) with water vapour.*

Omitting point 14, all desorption points, whether of the first set (8-13) or of the second set (19-20), fall on a curve which is slightly convex to the $\log q$ axis (*cf.* experiment 2).

The reason for the initial sorption curves in experiments 1 and 5 lying above the desorption curves obtained at a later stage in the experiments obviously called for closer investigation. One possibility was that the pressure differences observed between the initial and the later readings were due to the presence in the gas space, when the former readings were being taken, of gases displaced from the charcoal, these being removed during the subsequent desorptions. It was indeed not very likely that such was for the case, for--

- (a) the pressure differences were of the same order in the two experiments, although the means used for removal of displaced gases during charging were certainly more efficient in experiment 5 than in experiment 1 ;
- (b) the pressure differences were relatively very considerable ; thus, in experiment 5, if they were entirely due to displaced gas, this spurious pressure would amount to 80-90 per cent. of the total pressure read off on the initial sorption curve at $q = 50$ mg./gram, and to 50-60 per cent. at 80 mg./gram.
- (c) all pressure readings plotted were definite in the sense that they remained unaltered, within the experimental error, when, after making a measurement, the gas space was pumped out and the pressure renewed by loss of vapour from the charged charcoal. It seemed very improbable that this would be the case if the charcoal had to give up to the vapour phase amounts of carbon tetrachloride and of some foreign gas of about the same order of pressure.

The occurrence of hysteresis with charcoal D during the resorption cycle suggested that possibly the effect was merely one of velocity, and that the establishment of equilibrium was a slow process. Consequently it was decided to study over a period of time the pressure developed by a charged specimen of the charcoal. At this stage, in addition, the technique employed† for the

* See 'J. Phys. Chem.,' vol. 33, pp. 1682, 1694 (1929).

† Part I, pp. 353-355.

estimation of the partial pressures of the various gaseous impurities present in the carbon tetrachloride vapour was first introduced.

Experiment 6.—A sample of charcoal D, evacuated at 110° , was charged at a temperature of 70° C. with carbon tetrachloride to a q value of 84.6 mg./gram. The steady pressure developed at 25° C. was measured and analysed, immediately after charging, and again at intervals for nearly 3 weeks. The results are contained in Table I, all pressures being given in millimetres of mercury.

Table I.

Time (in days) after charging.	Pressure of CCl_4 .	Pressure of CO_2 .	Pressure of permanent gas.
0	3.6×10^{-2}	Zero	Trace
1	1.9	Not measured	2.0×10^{-4}
3	1.45	2.0×10^{-2}	1.5
4	1.30	2.2	1.0
13	1.19	3.3	3.0
19	1.10	4.4	2.0

The carbon tetrachloride pressure is seen to fall steadily, being only 30 per cent. of the original figure 19 days after the charging process. The permanent gas (CO ?) pressure is small and almost constant within the experimental limit of error, but the carbon dioxide pressure rises just as steadily as the carbon tetrachloride pressure falls. The conclusions to be drawn are (i) that the initial sorption pressures measured in experiment 5, and probably also in experiment 1, are true carbon tetrachloride pressures and are not appreciably in error owing to the presence of foreign gases, and (ii) that there is a "lag" in the setting up of equilibrium which is connected with the slow displacement of carbon dioxide from the charcoal by carbon tetrachloride and, until this displacement has been completed, true equilibrium figures cannot be expected.

The initial and final carbon tetrachloride pressures observed in this experiment are plotted in fig. 4 (squares). Both of them lie above the corresponding initial and final pressures obtained in experiment 5 for the same q value.

As evacuation at 110° C. had failed to free the charcoal thoroughly from carbon dioxide held on its surface, it was decided to try the effect of a higher degassing temperature, the object still being to obtain a reversible isothermal commencing with low charges of sorbate.

Experiment 7.—A specimen of charcoal D was degassed at 270° C., carbon tetrachloride admitted in the usual way to a q value of 7.54 mg./gram, the

displaced gases evacuated, and the pressure measured. Four more sorption points were determined (point 5 = 107.2 mg./gram), then six desorption points, and a final resorption point (No. 12 = 75.4 mg./gram). The results are plotted in fig. 4 (triangles and broken curve). It will be seen---

- (a) that the first sorption points still lie above the later points, though to a lesser degree than in experiment 5;
- (b) that the desorption points 6-11 lie on a curve which is very slightly convex to the $\log q$ axis, or, alternatively, that points 7-10 lie on a straight line;
- (c) that the desorption points are very close to, but at slightly lower pressures than the desorption points of experiment 5;
- (d) that the resorption point 12 shows very slight hysteresis, negligible in comparison with that shown by points 15 f.f. of experiment 5.

One interesting feature of this experiment was that at no stage was there any measurable pressure of carbon dioxide in the gases. On the other hand, the permanent gas pressures were of the order of 10^{-3} mm., as compared with 10^{-4} mm. found in experiment 6, and therefore presumably present in experiment 5. It therefore would seem probable that it is the slow displacement of any gas which may be held on the charcoal surface, and not specifically the displacement of carbon dioxide, which is responsible for the irreversibility of these isothermals. That carbon dioxide was still present in the vapour phase in experiment 7, although in such small amounts as to be undetectable by the usual procedure, was shown by condensing and examining the vapour evolved when passing from one desorption point to another. Thus, after point 8 had been determined, the charcoal was desorbed at 60° prior to measuring point 9. Two charges of vapour were condensed out and examined during this process. In the first, about 5×10^{-3} mm. of carbon dioxide were found, associated with about 1.5 mm. of carbon tetrachloride, or one part in three hundred. In the second charge, taken from the apparatus after $1\frac{1}{2}$ hours at 60° , the carbon dioxide pressure was about 10^{-2} mm., or double the first figure, corresponding to the longer time allowed for its displacement from the charcoal.

As an evacuation temperature of 270° had not proved successful in completely eliminating carbon dioxide, a still higher temperature was tried.

Experiment 8.—A specimen of charcoal D was degassed at 800° C., charged to 29.1 mg./gram and the first sorption point measured. Five more sorption points were obtained (point 6 at 110.0 mg./gram) followed by three desorption points (point 9 = 58.6 mg./gram). The results are shown in fig. 4 (circles

and dotted curve). The sorption points are irregular but, as before, lie at higher pressures than the desorption points, whilst falling below the sorption points obtained after evacuation either at 110° or at 270° . Points 6-9 lie on a curve practically coincident with the desorption curve of experiment 7.

The permanent gas pressures measured in this experiment were of the same order (10^{-3} mm.) as in experiment 7. But *no* carbon dioxide could be detected, either during the separate pressure measurements, or even when a considerable amount of vapour was condensed out and examined during the determination of the desorption points as was done in experiment 7.

As attempts to obtain reversible isothermals commencing with low carbon tetrachloride charges had failed, we reverted to the procedure of experiments 2-4, *i.e.*, giving the charcoal a comparatively high initial charge and subsequently determining first a series of desorption points. At this stage in our work we began to use a more sensitive voltmeter* for the measurement of pressures below 10^{-3} mm., and in addition introduced for the first time certain improvements in technique† which considerably increased the accuracy of these low pressure measurements.

Experiment 9.—A specimen of charcoal E was degassed at 110° , charged up with carbon tetrachloride to about 135 mg./gram, and desorbed to 129.2 mg./gram, at which figure the first pressure reading was taken. Prior to this, very large amounts of displaced carbon dioxide had been eliminated. Nine further desorption points were measured (point 10 = 11.7 mg./gram), followed by six resorption points (point 16 = 102.1 mg./gram) and finally by two desorption points (No. 18 = 81.7 mg./gram). The results are plotted in fig. 5 (first desorption series as squares, resorption points as circles, last two desorption points as crosses). In this case, whilst points 1-4 lie fairly closely on a straight line, the desorption points 1-8, taken as a whole, again form a curve slightly concave to the $\log p$ axis. Points 9 and 10 are displaced to rather lower pressures than would correspond to a continuation of the curve just mentioned. Together with the resorption points 11-16, they fall on a curve which lies very near to the first desorption curve, but at slightly lower pressures. This type of behaviour is quite different from that found in experiment 5. There is an indication that the second set of desorption points would be at still lower pressures.

The incomplete reversibility of the isothermal obtained in this experiment, unexpected after the results of experiments 2-4, suggested that, whilst in the

* Part I, p. 348.

† *Ibid.*, p. 357.

latter the preliminary heavy charge of carbon tetrachloride had sufficed to remove practically all the carbon dioxide from the charcoal surface, this had

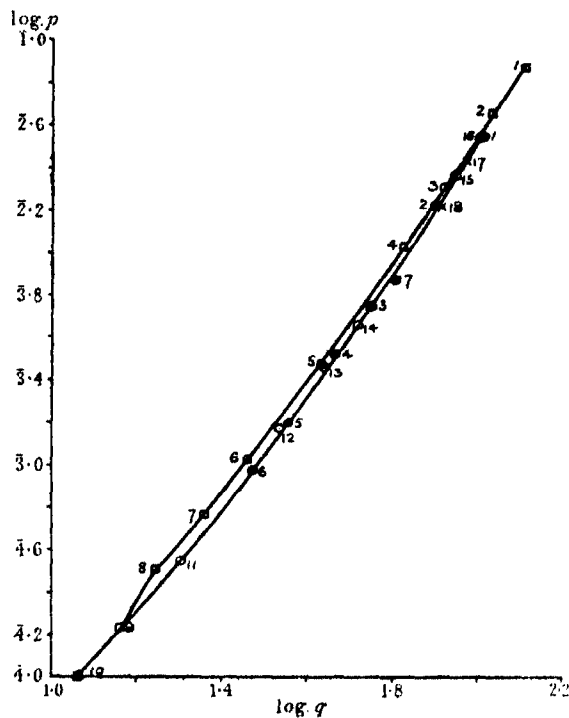


FIG. 5.

not been so in the present case. This suggestion was confirmed in a rather striking way by the result of the analysis of the vapour phase found in equilibrium with the charcoal at point 14 (52.4 mg./gram). Whereas up to point 13, the amounts of carbon dioxide found in the vapour had been low (of the order of 10^{-4} mm.), at point 14 a sudden liberation of this gas seemed to take place, the pressure measured being 100–200 times the pressures previously observed, and indeed considerably exceeding the carbon tetrachloride pressure. The actual figures for points 13 and 14 are in the following table.

Table II.

Number of point.	Charge in mg./gram.	Pressure of CO_2 in mm.	Pressure of CCl_4 in mm.
13	43.7	2.5×10^{-4}	2.66×10^{-3}
14	52.4	3.7×10^{-3}	4.50×10^{-3}

Unexpectedly, however, this rush of carbon dioxide was not accompanied by a break in the resorption curve and by an appreciable increase in sorption capacity, as reference to fig. 5 will show. It would indeed rather appear as if the increase in sorption capacity had taken place earlier, between points 8 and 9, *i.e.*, as if, at this stage in the experiment, the carbon dioxide had been effectively displaced by the carbon tetrachloride from close association with certain parts of the charcoal surface which, up to then, it had been denying to the carbon tetrachloride, but that this displaced gas had only been completely liberated from the charcoal surface later, when the carbon tetrachloride concentration, or pressure in the gas phase, had reached some kind of a critical value. A similar sudden development of relatively high permanent gas pressures, occasioned by the carbon tetrachloride content of the charcoal rising above a certain critical figure, has been noticed in another connection.

For the next experiment, it was decided to revert to evacuation at 800° , in order to see whether the "drift" of the resorption curve towards lower pressures found with this charcoal could be avoided by more thorough degassing.

Experiment 10.—A specimen of charcoal F was degassed at 800° C., and a long series of readings taken, commencing with the low q value of 25.5 mg./gram. Eleven more sorption points brought q up to 347.2 mg./gram, and the pressure up to 0.227 mm., a higher figure than we had up to then measured on the Pirani gauge. Then followed 13 desorption points, the lowest (No. 25) having a q value of 60.8 mg./gram, and finally four resorption points ($29 = 156.8$ mg./gram).

The results are shown in fig. 6 (sorption crosses, desorption circles, resorption triangles). The sorption points up to No. 11 lie smoothly on a line which is very slightly convex to the $\log q$ axis. Point 12 appears to deviate from this line in the direction of lower pressures. This deviation becomes more marked when the desorption points are considered. These, as usual, lie at lower pressures than the sorption points. Numbers 14–21 fall on a straight line, which the line drawn through 12 and 13 cuts at $\log p = 2.98$, or at a pressure of 0.096 mm. Omitting point 22, which would appear to be in error, the remaining desorption points (23–25) fall away below the straight line in a manner similar to that observed in experiment 9. The resorption points, commencing with 27, lie at very slightly lower pressures (*cf.* experiment 9), *i.e.*, the higher evacuation temperature has not in this case completely eliminated drift. As in experiment 8, no trace of carbon dioxide was found in the

vapour phase, whilst the permanent gas pressures were of the order of 10^{-3} mm.

The only experiments up to this point which threw any light on the influence of the preliminary evacuation temperature were numbers 5, 7 and 8 (charcoal D), the conclusion being that the effect on the initial low quantity sorption

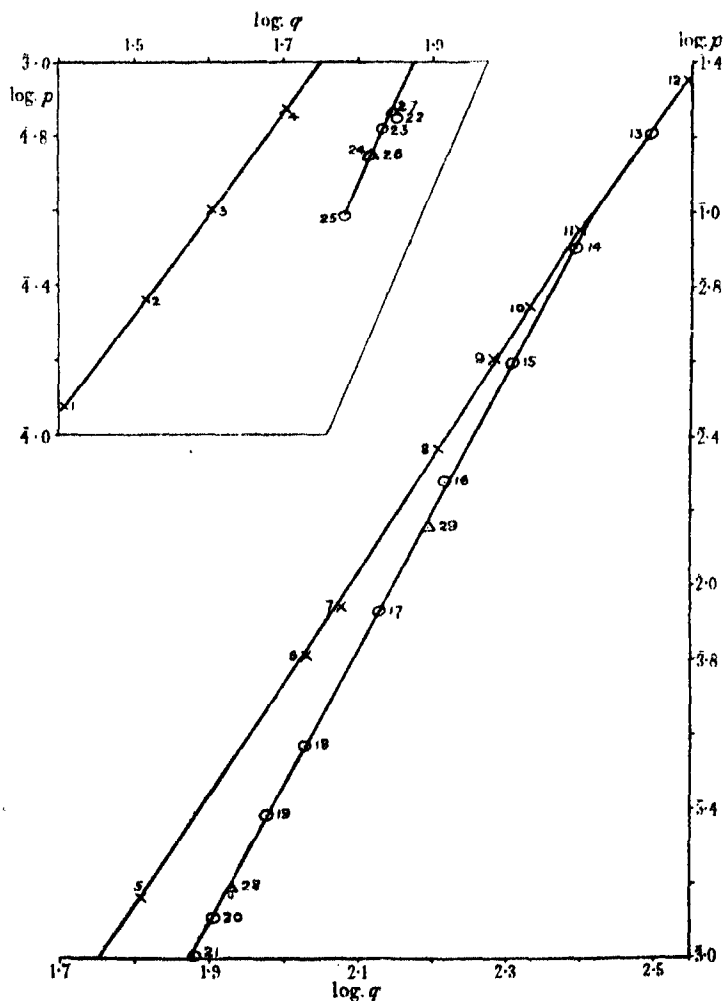


FIG. 6.

curve was considerable and on the final desorption curve slight, in both cases a higher evacuation temperature leading to lower pressures for the same q value. To test this point further, the next experiment was done.

Experiment 11.—A sample of charcoal C was degassed at 800° , charged initially to at least 270 mg./gram, and then a series of 11 desorption points taken (extreme q values 265.5 and 76.5 mg./gram). The results are shown in fig. 1 (circles and dotted curves). The first eight points lie on a satisfactory straight line, whilst the last three, as in experiments 9 and 10, lie at pressures falling below this line. No trace of carbon dioxide was found, and the permanent gas pressures were only about 10^{-4} mm. The interesting result is that, in this case, the desorption curve lies at considerably higher q or lower p values than was found with the same charcoal outgassed at 110° (experiments 1 and 2). Attention should, however, perhaps be drawn to the fact that the maximum charge put into the charcoal in this experiment (270 mg./gram or more) exceeded that employed either in experiment 1 (260 mg./gram) or in experiment 2 (160 mg./gram).

At the conclusion of this experiment, the charged charcoal of point 11, holding 76.5 mg./gram, was used for the first of a series of isostere measurements (see Part III).

(2) *Isothermals Derived from Isostere Measurements.*

In addition to the above directly determined isothermals, a number were derived from the isostere measurements described in Part III, by taking the pressures corresponding to the intercepts made by the line $1/T$ (where T is 298° K.) when drawn through the different linear $\log p - 1/T$ plots, and combining these with the q values characteristic of the different isosteres. Such isothermal points will be found in figs. 1–5 (no isostere measurements were made with charcoal F) and are in every case denoted by solid black circles.

Fig. 1 (charcoal C) contains three such isothermals. The first (dotted curve), for charcoal degassed at 110° , is definitely irreversible. Its points lie in the same general p/q region as those of experiment 2, but show a continual tendency to work down to lower pressures. Point 5 is seen to be missing. Between points 4 and 6, the charcoal had been charged up to 313 mg./gram of carbon tetrachloride and the isostere determined, but only over a temperature range below 25° C. Extrapolation of the isosteres to pressures exceeding 0.1 mm. is inadmissible (see Part III). The second isothermal, for charcoal evacuated at 800° (continuous curve, point numbers 1', 2', etc.), really forms a continuation of the isothermal of experiment 11, and sets out from point 11 of that experiment. It is seen to lie at slightly lower pressures than were observed in experiment 11, and its last point (No. 7') shows very considerable

drift in the direction of still lower pressures. It was noticed that, when desorbing down to this last q value, comparatively large amounts of permanent gas were set free. The third isothermal (continuous curve, point numbers 1'', 2'', etc.), also for charcoal evacuated at 800°, was obtained by commencing with the very small charge, for this charcoal, of 28.3 mg./gram. The lowest actually measured pressure in this case was 10^{-3} mm. at a temperature of 36° C., but the isostere allowed of accurate extrapolation to 25° C., the pressure found being about 1.8×10^{-5} mm. The five points of this isothermal, all sorption points, lie below the sorption isothermal of experiment 1 (charcoal degassed at 110°) and above the desorption isothermal for the 800°-evacuated charcoal (experiment 11). The relations are in fact similar to those shown in fig. 4 for charcoal D. It will be seen that the isothermal is somewhat concave to the $\log q$ axis, the only case of the kind noted by us.

Fig. 2 contains a single derived isothermal (broken curve) for charcoal A evacuated at 110° C. It is not reversible, tending towards lower pressures on its desorption branch. Except for the two points with the highest q values it lies below the isothermal of experiment 3.

In fig. 3 is an isothermal (for 110°-evacuated charcoal B) consisting of two desorption branches and of 17 points in all (broken curve). The first branch commences with a q value of 84.5 mg./gram, and comprises 12 points, finishing at 10.5 mg./gram. It lies just above the isothermal of experiment 4 at its commencement, but soon crosses the latter. Its points fall on a curve which is nearly linear, but with the usual slight convexity to the $\log q$ axis at higher pressures. The second branch commences with the high charge, for this charcoal, of 164.4 mg./gram and with a pressure of 0.184 mm. It shows a break at 0.11–0.12 mm., and then proceeds in such a direction as to be practically parallel to and nearly continuous with the low pressure linear portion of the first branch. The last point (No. 17) happens to have the same q value (84.5 mg./gram) as the first point of the first branch, and its pressure is 0.041 mm. as against 0.0453 mm.

Fig. 4 contains, plotted on a continuous curve, four derived isothermal points for charcoal D evacuated at 110°, all being at comparatively high q values, and falling on a line which is practically parallel to the general direction of the various desorption curves for this charcoal.

Fig. 5 contains a derived isothermal for charcoal E (evacuated at 110°) consisting of seven points, of which six are desorption points, commencing with 103.4 mg./gram, and the last a resorption point. The form of the isothermal is very similar to that of experiment 9, the points tending to lie

on the resorption curve for that experiment. The resorption point exhibits a tendency towards still lower pressures.

(3) *Comparison between the Isothermals of the different Charcoals.*

The relative sorptive properties of the six charcoals investigated between the pressure limits of 0.1 and 0.001 mm. of mercury are shown in fig. 7, where p is plotted against q . The actual points plotted are:—

- A (110°) Points 1-9 of experiment 3.
- B (110°) Points 1-8 of derived isothermal.
- C (800°) Points 1-9 of experiment 11.
- D (110°) Points 10-13 and 20 of experiment 5, together with the four points of the derived isothermal.
- E (110°) Points 1-6 of experiment 9.
- F (800°) Points 14-21 of experiment 10.

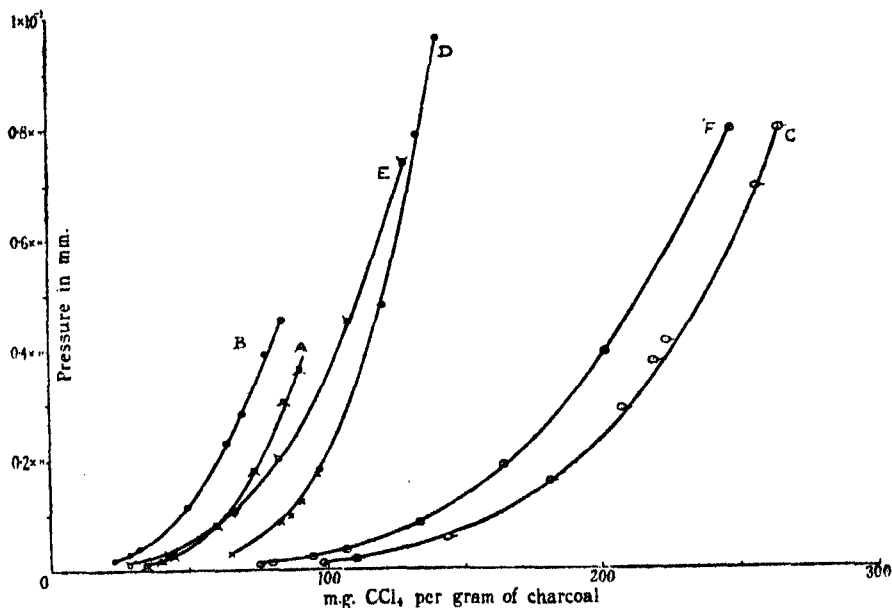


FIG. 7.

Although the evacuation temperatures are not the same in every case, reference to figs. 1 and 4 will make it clear that the relative positions of the different charcoals are only slightly affected by this circumstance. Two points call for notice. The steam-activated nut charcoals appear to be the best absorbents for carbon tetrachloride in this pressure region under our

conditions of work, and the fact that the isothermals cross or tend to cross shows that these relative sorption efficiencies are a function of the pressure of the carbon tetrachloride vapour.

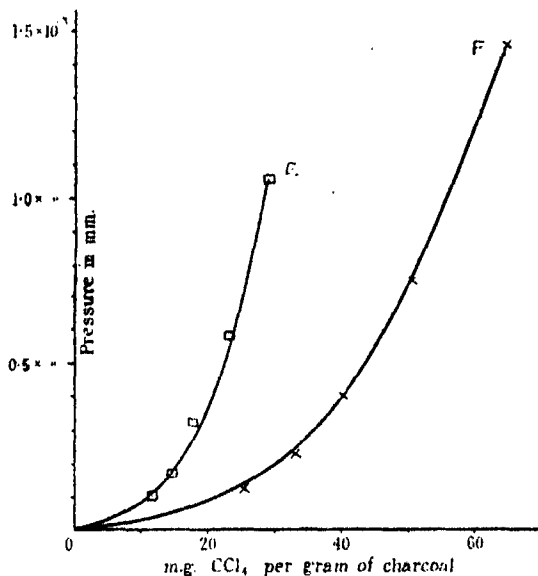


FIG. 8.

Fig. 8, containing data given by charcoals E and F, shows the type of result experimentally possible at low pressures when using the more sensitive volt-meter.

The Sorption of Carbon Tetrachloride at Low Pressures by Activated Charcoals. Part III.—Isosteres—Discussion.

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(1) *Isosteres.*

The essential aim of these measurements of the dependence of equilibrium pressure on temperature for charcoals with definite charges of carbon tetrachloride was the calculation of heats of sorption by the Clapeyron-Clausius equation. This was effected by plotting each isostere in the form of the logarithm of the pressure against the reciprocal of the absolute temperature, the slope of the resulting linear curve measuring the molecular heat of sorption.

A few points regarding experimental detail will be briefly referred to. The number of pressure-temperature measurements made on each charged charcoal sample varied between 3 and 13. As each pressure measurement involved opening up the charcoal container to the pressure gauge and connecting tubes (of total volume about 330 c.c.), this space was, prior to turning the container tap, charged with carbon tetrachloride vapour from the supply bulb until its pressure was near to (although still below) the pressure which it was estimated the charged charcoal would exert at the temperature in question. In this way, loss of sorbate from the charcoal during the set of measurements, which might have proved appreciable without this precaution, was reduced to a quite negligible figure.

The temperature variation was effected by immersing the charcoal bulb in a small Dewar vessel containing water. For 0° C. crushed ice was added. Temperatures above room temperature and up to 90° C. were obtained by means of a small electric heater immersed in the water. Adjustments could rapidly be made and the temperature kept constant within 0.05° C. for the time required for making the measurement. In practice it was found that, whether the charcoal had previously been raised or lowered in temperature, the pressure adjusted itself to its new constant value within 15 minutes, and it is highly probable that this simply represented the time required for the setting in of thermal equilibrium.

The change from one charge to another, whether a sorption or a desorption, was carried out as in the isothermal determinations, and any carbon dioxide or permanent gas was measured and allowed for just as before. When once

the initial displacement of such gases had been effected, any particular isostere was found to be reversible, *i.e.*, the points fell on the same curve whether the temperature were rising or falling.

Fig. 1 contains two examples of groups of isosteres, in one of which sudden changes in slope are seen to occur on passing a pressure in the region of 0.1 mm. The numbering of the points indicates the order in which they were measured.

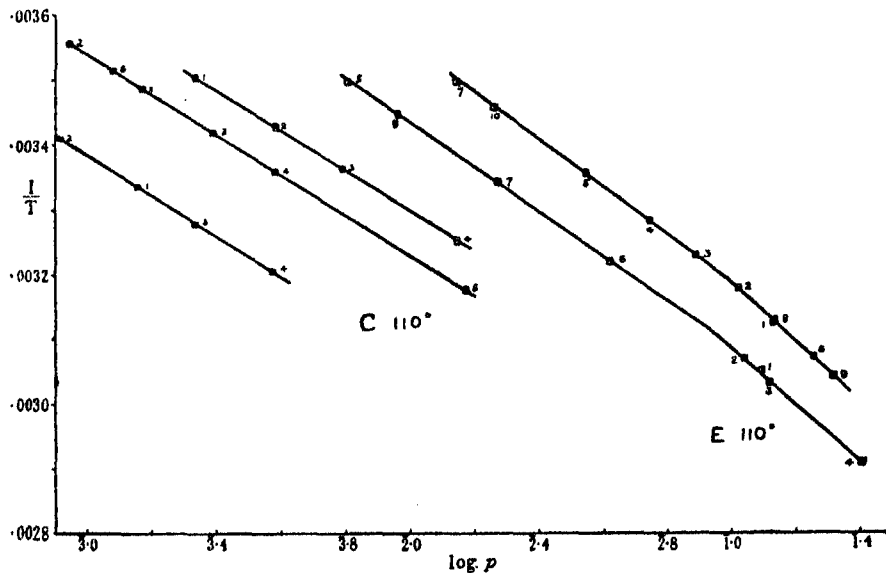


FIG. 1.

In each of the following tables are given, in kilo-calories, the values of the molecular heats of adsorption, calculated from the slopes of the isosteres, for differently charged specimens of the same charcoal. The order inside each table is the order in which the measurements were made. We think that the third significant figure given for λ is of definite value.

Table I.

Charcoal A. Degassed at 110°.

q in mg./gram.	λ in Cals.
55.2	14.6
51.1	14.6
92.4	13.5
87.6	13.8
87.0	14.5
40.3	15.8

Table II.
Charcoal B. Degassed at 110°.

q in mg./gram.	λ in Cals.	
	(a) At pressures below isostere break.	(b) At pressures above isostere break.
84.5	12.6	
78.5	12.8	
69.9	13.1	
64.2	13.2	
49.9	13.7	
32.5	14.3	
29.0	14.45	
23.5	14.6	
18.3	14.6	
15.4	14.6	
13.8	14.6	
10.5	15.7	
164.4	10.4 ?	8.8 (0.12 mm. ?)
148.3	11.4	8.95 (0.093 mm.)
129.7	11.4	9.0 (0.097 mm.)
106.1	12.0	9.5 (0.090 mm.)
84.5	12.7	9.9 (0.090 mm.)

Table III.
Charcoal C. Degassed at 110°.

q in mg./gram.	λ in Cals.
89.1	14.6
63.4	14.6
114.1	14.6
159.0	14.1
313.0	11.8
243.1	12.8
229.6	12.8

Table IV.
Charcoal C. Degassed at 800°. Series 1.

q in mg./gram.	λ in Cals.
76.5	15.7
132.2	14.1
147.6	14.2
182.2	14.0
210.2	13.7
200.0	13.9
97.9	16.6

Table V.

Charcoal C. Degassed at 800°. Series 2.

q in mg./gram.	λ in Cals.
28.3	17.3
56.6	15.7
95.6	14.8
147.6	13.6
162.5	13.9

Table VI.

Charcoal D. Degassed at 110°.

q in mg./gram.	λ in Cals.	
	(a) At pressures below isostere break.	(b) At pressures above isostere break.
134.1	12.2	10.0 (0.096 mm.)
120.9	12.0	10.9 (0.084 mm.)
97.5	13.2	
141.2	12.1	

Table VII.

Charcoal E. Degassed at 110°.

q in mg./gram.	λ in Cals.	
	(a) At pressures below isostere break.	(b) At pressures above isostere break.
103.4	12.6	10.2 (0.093 mm.)
79.7	13.3	10.4 (0.093 mm.)
56.3	14.2	
46.5	14.6	
35.9	14.6	
29.8	15.1	
63.5	14.1	12.0 (0.05 mm. ?)

No isostere measurements were made with charcoal F.

The figures in the above tables, omitting the λ values observed at the higher pressures, are plotted in fig. 2, the numbering of the points corresponding to the order in the tables. Whilst they differ from one another in detail very

considerably, the data for charcoals degassed at 110° suggest the following general conclusions. Commencing with high q values, the heat of sorption

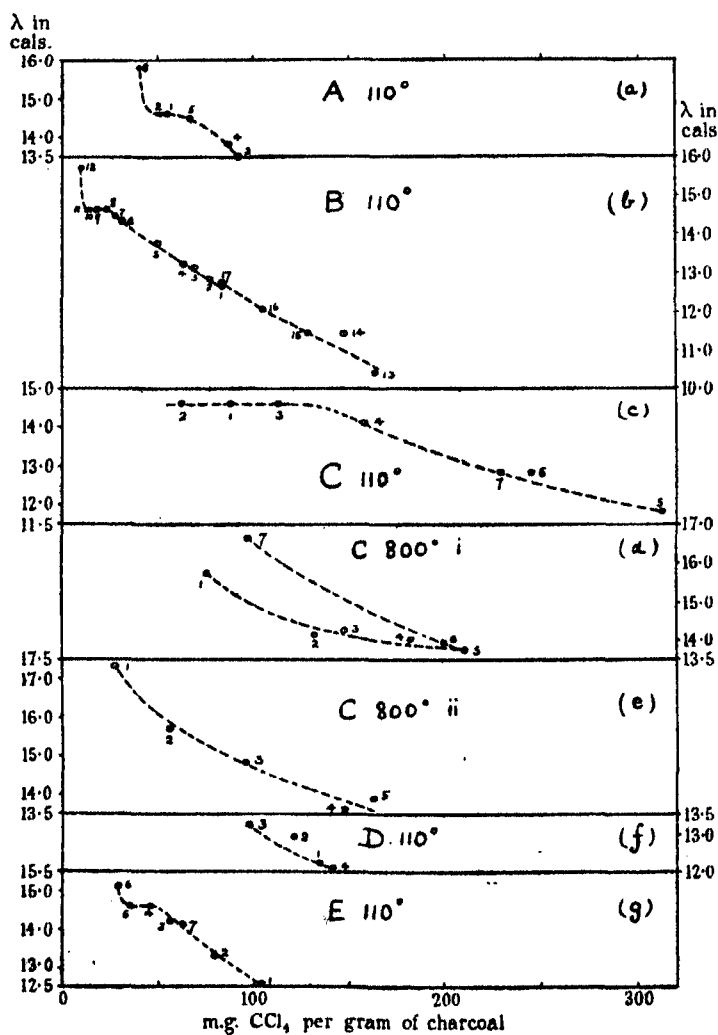


FIG. 2.

increases (in every case) more or less linearly (B, C, E) with decrease in q until a λ value of about 14.6 cal/g is reached. It then remains practically constant at this figure over a q range which varies from charcoal to charcoal, not exceeding 10–20 mg./gram with A, B and E, but amounting to at least 50 mg./gram with charcoal C. Finally, as q becomes still lower, λ again begins

to rise (A, B, E) and rather more steeply than was the case at higher q values. The $\lambda - q$ curves appear to be reversible within experimental error; and the last point obtained for charcoal B, where the q value chanced to coincide with that of the first point of the series, also gave a practically identical λ value.

The only charcoal worked with after degassing at 800° was C, on which two experiments were performed. These were the first isosteres measured, and may on that account be subject to experimental error, although this is not apparent in the separate $\log p/T^{-1}$ plots. Nevertheless, we feel justified in suggesting provisionally that the 800° C. evacuation has appreciably modified the nature of the $\lambda - q$ curve for charcoal C. Instead of this having the detailed structure mentioned above, it appears to consist of a continuous curve, of which the slope, increasing as the q values become smaller, is less at high q values than was the case with the charcoal evacuated at 110°. The constant λ section of the curve given by the latter charcoal has either disappeared, or else is shorter, and characterised by an altered λ value. Moreover, the curve tends to be irreversible, as shown by point 7 of Series 1 (Table IV). The highest λ values observed are considerably greater than those noted with any charcoal outgassed at 110°. Finally, the curve obtained in Series 1 (Table IV), where the charcoal had previously been charged up to at least 270 mg./gram (see Part II, experiment 11) before any isostere measurements were made, lies above that of Series 2 (Table V), where the first readings were made immediately after a first charge of 28.3 mg./gram.

As already mentioned, and as indicated in the tables and in fig. 1, breaks were observed in certain of the isosteres. These were nearly all found in the region of 0.1 mm., and were invariably obtained if the number of points at pressures higher than this figure sufficed to define the slope of the isostere. The actual pressures at which these breaks occur, measured by the point of intersection of the two branches of the isostere, are given in the tables. It must be realised that their values cannot be defined with any great exactness by this method, being considerably affected by a slight error in judgment in drawing the "best" lines through the isostere points. Thus, when the isosteres for the first two q values in Table VII were first drawn out, the breaks were found in the region of 0.06–0.07 mm., instead of at 0.09–0.10 mm. Another example is furnished by the data for $q = 164.4$ mg./gram in Table II, where both the low pressure λ value and the pressure of the break are open to considerable doubt, there being evidence that the nature of the charcoal surface was changing during the measurements.

These remarks, however, do not affect the question of the *existence* of the breaks, on which matter there is no doubt. A further important fact* is that they occur in the same pressure region in which a break was found (at 0.096 mm.) during the determination of the isothermal at 25° C. for charcoal I' degassed at 800° (Part II, experiment 10).

(2) *Discussion of Experimental Results.*

Our experiments have made clear (and, as we think, for the first time) the great effect exerted on the nature of the sorption isothermals of vapours on charcoal by traces of gases present on the surface of the sorbent. For charcoals previously evacuated at 110° C., the disturbing gases have been shown to be displaced from the charcoal surface chiefly as carbon dioxide, accompanied by smaller quantities of some permanent gas. A sufficiently high evacuation temperature has as result the complete absence of carbon dioxide, but usually leads to the appearance of larger quantities of the permanent gas. Thus, the gases displaced when the sorbate is first admitted to the charcoal are preponderatingly carbon dioxide with "110° C." charcoals, and permanent gas with "800° C." charcoals. The point under discussion is also illustrated by the following table, showing the approximate pressure in millimetres of foreign gases found in the "equilibrium" vapour phases during the different isothermal experiments of Part II.

Table VIII.

Experiment.	Charcoal.	Evacuation temperature.	CO ₂ .	Permanent gas.
		° C.		
6	D	110	10 ⁻³	10 ⁻⁴
9	E	110	10 ⁻⁴	Usually quite negligible
		*	(in one case 10 ⁻³)	
7	D	270	Trace	10 ⁻³
8	D	800	Absent	10 ⁻³
10	F	800	Absent	10 ⁻³
11	C	800	Absent	10 ⁻⁴

Although we have not tested the matter, we feel justified in assuming the permanent gas to be essentially carbon monoxide, with perhaps a trace of

* The discovery of a break at 0.11-0.12 mm. in the "derived" isothermal for charcoal B (Part II, fig. 3) does not, of course, constitute further independent evidence for the existence of these discontinuities, as the presence of such breaks in the isosteres (Table II) naturally necessitates their reproduction in any isothermal which is carried up to the critical pressure of their appearance.

hydrogen. There seems little doubt that the gases displaced by the sorbate are identical with those which would ultimately have been removed if the preliminary evacuation process had been continued for a considerably longer time (the sorbate is far more effective in this respect than the high temperature evacuation). And it has been shown* in the particular case of charcoal C (i) that increase of evacuation temperature to 800° results in a far higher CO/CO₂ ratio in the resulting gases and (ii) that, at 800°, this ratio increases during the last stages of the evacuation.

In any case, whatever their nature, the increasing degree of removal of these gases during the course of an experiment is normally accompanied by a gradual drift of the isothermal towards higher q and lower p values.

In addition, certain changes in the shape of the isothermals take place. If small quantities of sorbate are progressively admitted to a freshly evacuated charcoal surface, irreversible isothermals, markedly convex to the $\log q$ axis on the sorption branch, are obtained (Part II, figs. 1, 4). The higher the evacuation temperature, the less marked are both the convexity of the sorption isothermal and the degree of irreversibility (Part II, fig. 4†). With charcoals degassed at 800°, this convexity may almost disappear (II, 6) or the isothermal may even become somewhat concave to the $\log q$ axis (third derived isothermal in II, 1).

If, on the other hand, the charcoal be charged to a relatively high q figure before the first isothermal point is taken, then the resulting curve is far more nearly reversible, and only shows at the most a slight residual convexity to the $\log q$ axis (II, 1, 2, 3, 5). If the charcoal has been degassed at 800°, then the isothermal may even be somewhat concave to the $\log q$ axis at low pressures (II, 1). The same general statements hold for the desorption branches of those isothermals which start out from low q and p values. They are normally much less convex to the $\log q$ axis than are their original sorption branches and coincide fairly closely with subsequent resorption points‡ (II, 1, 4, 6).

These changes in position and in shape of the isothermals during the course of the experiments we imagine to be the direct result of the gradual elimination

* 'J. Phys. Chem.,' vol. 33, p. 1153 (1929).

† From this point onwards in references inserted in the text, a Roman numeral will denote the Part of this investigation, and an Arabic numeral, unless otherwise specified, will refer to a figure.

‡ It may be noted that, in experiment 1, of Part II (II, 1) if point 7 as plotted be assumed to be in error, and to lie at too low a pressure, the desorption branch of the isothermal may be drawn as a single continuous curve convex to the $\log q$ axis instead of as two linear portions intersecting at a definite angle.

of the gases from the charcoal surface. This elimination accompanies both sorption and desorption processes. It proceeds more rapidly at a high temperature and occurs to a certain extent irregularly. This last conclusion is based not only on the sudden evolution of gas noted in Part II, experiment 9, but also on the marked drift of point 7' in the second of the derived isothermals of II, 1, as well as on certain unpublished results. The elimination of carbon dioxide occurs relatively easily compared with that of carbon monoxide, whilst the liberation of very small quantities of the latter gas from the charcoal surface appears to have a comparatively big effect on the sorptive capacity of the charcoal.

To what extent any of our isothermals correspond with the *maximum* sorptive power of the charcoals in question, *i.e.*, to an absolutely clean charcoal surface, is difficult to say. In the case of charcoal A (II, 2) this is certainly not so. The derived isothermal shows drift, and further unpublished work has shown such drift to be very considerable with this charcoal. Point 7' in the diagram (II, 1) for charcoal C suggests that the limiting isothermal may lie to the right of those actually drawn. Charcoal F resembles C, and one may presume that drift is incomplete in II, 6. On the other hand, many experiments on chemically activated charcoals carried out in this laboratory indicate that the derived isothermal for charcoal B (II, 3) may well be near the limiting value; the position of the derived isothermal in II, 4, combined with the fact that the desorption and resorption points in experiments 7 and 8 (Part II) fall near one another, suggests that the 800° curve for charcoal D approaches the limiting isothermal closely; a similar conclusion may perhaps be drawn in the case of charcoal E (II, 5), in spite of the position of point 7.

A similar degree of doubt affects the question as to what is the normal characteristic shape of the limiting isothermal (clean charcoal). We are inclined to think that, at very low pressures, in some cases perhaps inaccessible to measurement by our technique, all isothermals will become more or less concave to the $\log q$ axis, as is the case with charcoals C and F after evacuation at 800° C. (II, 1, 6), and, further, that any residual convexity to this axis found in our isothermals at higher pressures will disappear as the charcoal surface becomes completely cleaned up, the isothermal in this region becoming either linear or slightly concave to the $\log q$ axis. This would indicate that the surface of charcoal E in our experiments was still far from being clean; it is, however, also possible that this charcoal (raw material, chiefly coal) has a lower essential adsorptive capacity than the others, and that the shape of its isothermal is truly characteristic.

At one stage we thought that, when once gas displacement had been completed, all isothermals plotted logarithmically would prove to be linear below 0.1 mm.; but the trend of the experimental evidence does not support this conclusion, although there is no doubt that, in most cases, the Freundlich equation does hold for practical purposes over a considerable pressure range.

(3) *Theoretical Discussion.*

In order to render more precise our views on the nature of the adsorption and gas displacement processes, it is first necessary to consider the nature of the adsorbing surface. We imagine a clean charcoal surface to be inhomogeneous in sorptive properties, *i.e.*, to consist of areas or spots of varying adsorption potential. No activated charcoal when first used is, in practice, a clean charcoal; whether by exposure to air or, during activation, to oxidising agents such as air or steam, its surface is *poisoned by the adsorption of oxygen*. This gas is held most strongly in the regions of high adsorption potential ("active centres"), and the charcoal is most effectively poisoned in such regions. These active spots may centre on the edges and corner atoms of carbon atom lattices (Taylor) or may be of the nature of molecular gaps in the lattice (Magnus).

In the matter of the nature of the adsorbed oxygen, we base our conception on the experiments and views of Rhead and Wheeler,* Langmuir† and Garner and his collaborators.‡ When oxygen is admitted to a clean charcoal surface, it becomes bound to this surface in one of a number of ways, depending on the local adsorption potential and hence on the nature of the surface at that point. Loosely held gas can be re-liberated as oxygen on evacuation at low temperatures. To remove gas which is more strongly held, higher evacuation temperatures are necessary, and the oxygen comes off as carbon dioxide, *i.e.*, a C-C linkage in the lattice rather than a C-O₂ union is broken. Gas adsorbed at the most highly active spots is only given off at still higher temperatures, and in the form of carbon monoxide, *i.e.*, two carbon atoms are torn out of the lattice per molecule of oxygen. The probability of any particular sub-microscopic element of the surface becoming freed from oxygen is, of course, always a function of temperature, but only for the loosely held gas is it a direct function of the original adsorption potential at that point; in other cases it depends rather on the average energy required to disrupt the local carbon

* 'J. Chem. Soc.', vol. 103, p. 461 (1913).

† 'J. Amer. Chem. Soc.', vol. 38, p. 2276 (1916).

‡ 'J. Chem. Soc.', vol. 125, p. 1288 (1924); p. 2451 (1927).

lattice. The result of the successive adsorption of oxygen and its desorption as an oxide of carbon will be to alter the surface structure and the local adsorption potential, and either an increase or a decrease of the latter can readily be imagined. But in general this alteration will not be great, and active centres will remain active centres, although with modified characteristics.

It is well known that the removal of the last traces of oxygen from a charcoal surface by evacuation, even at a high temperature, is very difficult. Our own work has shown that, during sorption experiments, measurable amounts of carbon dioxide and of permanent gas are liberated from charcoals previously degassed at 110° and at 800° respectively, a " 270° C." charcoal occupying an intermediate position. We think that the correlation between the composition of these gases and that of those liberated during evacuation of the charcoal, together with the fact that they are so slowly given off during the sorption experiments as to make it unlikely that they are present on the charcoal surface in the ordinary adsorbed state, indicates that they actually represent the residue of originally adsorbed oxygen which has remained on the charcoal despite the evacuation, and further shows that the competition for the active centres of some strongly adsorbed vapour, such as carbon tetrachloride, is a far more effective means of removing oxygen from these centres than is high temperature evacuation. It also indicates that the residual oxygen charge on a charcoal cooled down after outgassing is present as potential carbon monoxide or carbon dioxide, depending on the evacuation temperature.

Regarded in this light, the general nature of the results of our isothermal experiments is now clear. A freshly evacuated charcoal will have a residual oxygen charge occupying the regions of highest potential, its nature and density depending on the temperature and the thoroughness of the outgassing. Admission of vapour to the charcoal will primarily result in some sorbate going on to the charcoal at the points of highest available potential. These will be more numerous and potent with " 800° C." charcoals than with " 110° C." charcoals (a " 270° C." charcoal will be intermediate in this respect). Hence, as found, the initial q/p ratio will be greatest for " 800° C." charcoals. Adsorbed molecules have a certain degree of mobility on the sorbent surface,* depending on the intensity with which they are adsorbed.† In addition to this, the active centres occupied by the oxygen will be subjected to a molecular bombardment from the vapour phase. The result will be that, from time to

* Volmer, 'Z. Physik,' vol. 35, p. 170 (1925); Volmer and Adhikari, 'Z. Phys. Chem.,' vol. 119, p. 461 (1926).

† Polanyi and Welke, 'Z. Phys. Chem.,' vol. 132, p. 371 (1928).

time, carbon dioxide or carbon monoxide molecules will be turned out of the carbon lattice, and the active centres left vacant will be filled by sorbate molecules ; in other words, gas displacement from the charcoal will be accompanied by an increase in the sorbate q/p ratio, and the isothermals will drift in the way found. The effects of raising the temperature during sorption and desorption, of increased sorbate pressure during sorption, and of allowing the charged charcoal to stand (II, experiment 6), follow from what has been said and need no further elucidation. All will favour the liberation of gases from the charcoal, with a resulting drift in the isothermal or fall in the sorbate pressure. Only when the removal of oxygen is complete will this drift cease and the isothermal become truly reversible. And the final and definitive isothermals obtained with the same charcoal outgassed at a series of temperatures up to 800° C. (provided that the percentage of ash is not thereby affected), should differ from one another merely to an extent corresponding to any small variations in surface structure due to the liberation of the last traces of adsorbed oxygen as carbon dioxide in some cases and as carbon monoxide in others.

A few points call for special comment.

(1) Whilst oxides of carbon are slowly evolved from a charged charcoal standing at 25° C., and whilst there is ample evidence to show that any alteration or disturbance in the adsorbed layer (*i.e.*, not merely an increase, but also a decrease in the charge on the charcoal) facilitates the evolution of these gases, it seems that by far the most effective means of bringing about a complete oxygen clean-up is a high charge of the sorbate (carbon tetrachloride). This fact is responsible for the apparent, but false, reversibility noticed in certain isothermals when the initial charging pressure is not exceeded during the later stages of the experiment (II, 1, 3, 5).

(2) Some evidence exists for the view that carbon dioxide molecules, after their actual formation from the superficial carbon-oxygen complex by the displacing action of carbon tetrachloride, may exist on the charcoal in the ordinary adsorbed state for some considerable time during the measurements, provided that the carbon tetrachloride charge is kept low. In this way we may explain the sudden carbon dioxide evolution in experiment 9 of Part II ; the gas is *formed* at some moment between points 8 and 9, but is adsorbed by neighbouring active centres, vacant owing to the low carbon tetrachloride charge, before it can escape. When the carbon tetrachloride charge becomes sufficiently high (between points 13 and 14), it is displaced from these active centres, and hence from the charcoal.

(3) A similar view may be taken of the cause of the hysteresis observed in

experiment 5 (Part II). If, during the last stages of the desorption branch of the isothermal commencing with point 7 (II, 4), some of the carbon dioxide formed be imagined to be retained on the charcoal, and, being mobile, to pass from centres of lower to centres of higher potential as the latter are set free by loss of carbon tetrachloride, then, on resorption of carbon tetrachloride, hysteresis will result if the latter is incapable of displacing the carbon dioxide rapidly. (Such hysteresis was only found in the case of "110° C." charcoal D.)

(4) Another possible conception of hysteretic phenomena, bound up with a certain view of the greater adsorptive capacity normally shown at low pressures by charcoals outgassed at relatively high temperatures, is that some of the "pores" in the charcoal are only accessible with difficulty to the molecules of sorbate, owing to their small size and "remoteness," the process of sorption therefore taking time—and that such "pores" are more particularly those "made available" by the high temperature evacuation. The soundness of these ideas appears to us very doubtful, in view of the fact that all isothermals for a given charcoal, whatever the evacuation temperature, show a tendency to coincide at relatively high carbon tetrachloride pressures (II, 1, 4). It seems rather that all parts of the charcoal are spatially accessible to vapour with only a very short delay, and that the above-mentioned difference usually found at low pressures between low temperature and high temperature evacuated charcoals is due to a difference in clean-up of surface, as set out in this paper. In other words, sufficiently high pressures will cause adsorption of carbon tetrachloride on centres which are poisoned with oxygen in much the same manner as on cleaned-up adsorption centres; but such sorbed vapour will come off readily on reducing the pressure, whereas the vapour sorbed by a clean charcoal will not do so.

It may be added that our view of the nature of the effect of a high evacuation temperature on the sorptive properties of a charcoal, whilst being very similar to one at one time put forward by Magnus,* is quite different from the present views† of that author, with which we are in definite disagreement.

(5) The quantities of gases displaced from the charcoal are very small compared with the corresponding increases in the amounts of carbon tetrachloride taken up as a result of this displacement. It would seem as if the evolution of the oxides of carbon does not merely permit of adsorption on the

* 'Z. Anorg. Chem.,' vol. 155, p. 220 (1926).

† *Ibid.*, vol. 174, p. 142 (1928); vol. 184, p. 241 (1929).

spots previously physically covered with oxygen, but unmasks active centres capable of adsorbing relatively large quantities of carbon tetrachloride.

The views put forward in this discussion are also, in general, consistent with the results of our isostere measurements. High heats of adsorption are found associated with low q values (the sorbate first goes on to the high potential centres) and with an "800° C." rather than with an "110° C." charcoal (active centres freer from oxygen). The gradual displacement of gases in the course of an experiment is accompanied by a rise in λ (noticed when measuring the separate isosteres; compare also III, 2*d*, 2*e* and point 7 of III, 2*d*). Further, a comparison between II, 7, and III, 2 (corrected when necessary by reference to the direct and derived isothermals in II, 1-5) makes it clear that high adsorptive capacity at low pressures and high heats of adsorption are associated with one another in the same charcoal. The flattening out of the λ/q curves (III, 2) which occurs at a λ value of 14.6 cal. in the case of several of the charcoals evacuated at 110° seems to be associated with an active charcoal surface still poisoned by a certain amount of tenaciously held oxygen present as potential carbon dioxide, and the value of 14.6 cal. is perhaps characteristic of such a surface. The derived isothermals for "110° C." charcoals in II, 1, 2, are actually irreversible and further work in this laboratory has not confirmed the existence of this constant λ region in other cases.

The discussion of the breaks found in the isosteres and in Part II, fig. 6, will be reserved, as they appear to be a case of a more general phenomenon which has been observed and studied in this laboratory during the last few years. The question of the nature of the adsorption process is bound up with this discussion, and for that reason will not be dealt with here.

Summary of Parts II and III.

1. The results of determinations at 25° C. of low pressure adsorption isothermals of carbon tetrachloride on six different charcoals, using experimental methods already described, are communicated. The majority of these determinations were direct, but some isothermals were derived from isostere measurements.

2. The results of isostere measurements made for different charges of carbon tetrachloride on five of these charcoals are communicated, together with the heats of adsorption calculated from them.

3. At carbon tetrachloride pressures of about 10^{-1} mm., both the isothermals and the heats of adsorption exhibit a discontinuous change with further increase in pressure, in the direction of greater q/p and lower λ values respectively.

4. The influence on both isothermals and isosteres of the gradual displacement of gases from the charcoal surface during the processes of sorption and desorption is examined in detail.

5. The following conclusions are arrived at: (a) The adsorption potential of the surface of an activated charcoal varies from point to point; (b) all charcoal surfaces, and more particularly their high potential centres, are initially poisoned by a residual oxygen charge, which is gradually displaced in the form of carbon monoxide or carbon dioxide by the action of the sorbate; (c) the "drift" towards higher q/p ratios found experimentally during the determination of isothermals is due to this displacement; (d) no finally definitive results can be obtained until this displacement is complete; (e) such definitive isothermals are possibly only slightly dependent on the prior evacuation temperature of the charcoal (up to 800° C.); (f) the residual oxygen surface charge can sometimes cause hysteresis.

The measurements described in Parts II and III of this series were carried out between September, 1925, and March, 1927.

On the Absorption of Light by Gaseous, Liquid and Solid Xenon.

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(Received June 16, 1930).

[PLATES 13-17.]

INTRODUCTION.

1. *The Energy States of Oxygen Molecules.*

The results of studies made by McLennan and McLeod† and by McLennan, Smith and Wilhelm‡ on the Raman effects obtainable with liquid hydrogen have made it abundantly clear that molecules of hydrogen in the liquid phase exist or can exist in electronic, vibrational and rotational states that are exactly the same as states that are available for them to assume in the form of a gas or as isolated units. The same is true in regard to energy states that

* Student of the National Research Council of Canada.

† 'Trans. Roy. Soc. Canada,' vol. 22, p. 413 (1928).

‡ 'Trans. Roy. Soc. Canada,' vol. 23, p. 247 (1929).

molecules of oxygen or of nitrogen may take up when existing as isolated entities on the one hand or when existing as a gas or a liquid on the other.

In so far as oxygen is concerned, it is known from the work of Babcock that practically all the molecules of oxygen in the earth's atmosphere are in the electronic state of lowest energy possible for them to assume. Only a very small percentage of them, namely, 0.04 per cent., have even one quantum of vibrational energy. It has been shown by McLennan, Smith and Wilhelm that a similar statement applies in a description of the energy states of the molecules of oxygen as they exist in the liquid or in the solid phase. The band systems and the structures of the band systems that characterise the absorption spectra of gaseous, liquid and solid oxygen are identical. These bands all originate in transitions to higher energy states from rotational vibrational energy levels associated with a fundamental $^3\Sigma$ electronic energy state that can be shown by the theory of Hund and Mullikan to be the most stable one that molecules of oxygen can assume.

Although the energy levels are known that are available for the isolated or gaseous molecules of many substances, oxygen appears to be the only element for which certain energy states are known which the constituent molecules and atoms can assume when in the solid and liquid phases as well as when in the gaseous phase.

The three lowest electronic energy states in which oxygen molecules can exist are in order of magnitude $^3\Sigma$, $^1\Delta$, $^1\Sigma$. Of these $^1\Delta$ and $^1\Sigma$ are metastable. There is a higher $^3\Sigma$ electronic state known, but between it and the $^1\Sigma$ metastable state there exist three others designated for purposes of reference by McLennan, Smith and Wilhelm* as C, D and E. For these three the electronic configurations have not as yet been determined definitely.

These electronic energy levels are the ones involved in the production of the bands that characterise the absorption spectra of liquid and solid as well as gaseous oxygen.

With oxygen then, and probably also with other diatomic elements it appears to be clearly established that the electronic configurations giving rise to the normal energy levels of the molecules when isolated or in the gaseous state persist throughout the processes of liquification and solidification without any important or extensive disturbance or modification. It is perhaps of interest in this connection to point out that in liquid and solid oxygen we have an example of a perfect non-conductor or electrical insulator. So-called free electrons do not exist in ordinary gaseous, liquid, or solid oxygen.

* 'Trans. Roy. Soc. Canada,' vol. 24, p. 1 (1930).

2. *Metals, Liquid and Solid.*

For metals in the liquid or solid state but little is known as to the energy levels of the ions, atoms or molecules of which they are constituted. Absorption spectra and the phenomenon of metallic reflection reveal the existence of resonance frequencies, but what the entities are with which these frequencies are associated is not by any means evident. The wide absorption bands exhibited by very thin films of metals such as gold have a significance that must tell something of the state of the ultimate particles constituting the film, but the significance of these wide bands is not at all clear as yet. It is probable, however, that they are the manifestation of a set of resonance frequencies associated with some unique and well-defined frequencies of the isolated ions, atoms or molecules that go to make up the metal, for it is known that the conditions existing within a metallic solid are such as to give a wide distribution of energies about the normal energy levels of its constituent and elemental particles.

3. *Absorption of Mercury Vapour.*

From the work of Freed and Spedding, Wood and Guthrie, McLennan and Edwards* and of many others, we have learned something of the modifications produced in the absorption spectra of the vapours of metals and in those of the metal in the solid or liquid state brought about by changes of pressure and temperature. With a vapour an increase of pressure broadens the absorption bands and with solids the absorption bands generally become narrower when their temperature is lowered. With solutions an increase of concentration widens the absorption bands. Shifting of the bands towards the red end of the spectrum following an increase of pressure is another phenomenon observed with vapours.

With mercury vapour we have an interesting illustration of the selective absorption of radiations. Mercury atoms exist normally in a $^1S_0$ energy state. The next states higher into which they can be put by suitable excitation form a $^3P_{012}$ group. The next again above these is known as a $^1P_1$ or singlet P energy level. In accordance with the selection rules that apply the resonance frequencies are given by $h\nu_1 = ^1S_0 - ^3P_1$, and $h\nu_2 = ^1S_0 - ^1P_1$. To the former corresponds the resonance wave-length $\lambda = 2536.72 \text{ \AA}$. and to the latter the wave-length $\lambda = 1849.6 \text{ \AA}$. These two wave-lengths are the ones

* Freed and Spedding, 'Phys. Rev.', vol. 34, p. 945 (1929); Wood and Guthrie, 'Astrophys. J.', vol. 29, p. 24 (1909); McLennan and Edwards, 'Trans. Roy. Soc. Canada,' vol. 9, p. 167 (1915).

that are most readily absorbed by mercury vapour. Of the two $\lambda = 1849.6 \text{ \AA.}$ is more readily absorbed than $\lambda = 2536.72 \text{ \AA.}$ The reproduction shown in fig. 1 (Plate 13), which is taken from a paper by R. W. Wood,* shows the absorption corresponding to $\lambda 2536.72 \text{ \AA.}$ obtained with mercury vapour with increasing temperatures and pressures. It will be seen that the band is sharply delineated on the short wave side and that on the long wave side it is widened out more and more with increasing pressures.

In the reproduction shown in fig. 2 (Plate 13) which is taken from a paper by McLennan and Edwards (*loc. cit.*) this band is also in evidence, but it will be seen that the absorption band associated with the wave-length $\lambda 1849.6 \text{ \AA.}$ is much the wider and very much the more marked for corresponding pressures. Moreover it will seem that the $\lambda 1849.6 \text{ \AA.}$ band develops symmetrically with increase of vapour pressure. It appears to have widened out just as much on the short wave side as on the long wave side of the wave-length $\lambda = 1849.6 \text{ \AA.}$ when the pressure of the absorbing vapour was increased.

It is generally considered that the vapour of mercury is monatomic, and this raises a question as to whether or not the atoms of mercury remain unassociated when the vapour is condensed to a liquid and again when the liquid mercury becomes solidified. If the atoms of mercury under these circumstances remain unassociated would very thin films of liquid mercury or of solid mercury exhibit absorption bands corresponding to the two wave-lengths $\lambda 2536.72 \text{ \AA.}$ and $\lambda 1849.6 \text{ \AA.}$? If they would, then what would be the widths of these bands and how would the groups of waves constituting them be related to the two wave-lengths $\lambda 2536.72 \text{ \AA.}$ and $\lambda 1849.6 \text{ \AA.}$? Clearly if this information could be secured, it would be of assistance to us in identifying the unique and fundamental frequency with which all the resonance frequencies are associated that are involved in the production of an absorption band of the kind obtainable with films of metals such, for example, as gold and silver.

Attempts have been made by one of us, as well as by others, to see if well-marked and clearly defined absorption bands could be obtained with thin films of mercury of varying thickness, but none appear to have been observed so far that can be associated in a definite way with the resonance wave-lengths of mercury $\lambda 2536.72 \text{ \AA.}$ and $\lambda 1849.6 \text{ \AA.}$

It has become possible, however, to make progress with the solution of the problems involved in the absorption of light by mercury in its three phases by proceeding on somewhat different lines. The use of the monatomic inert gases in place of mercury makes the problems easier of solution, for with these

* "Effect of Foreign Gas on Spectral Lines," 'Astrophys. J.,' vol. 26, p. 41, 1907.

gases, with the possible exception of helium, it is safe to assume that the atoms remain loosely bound in all phases, and consequently the absorption bands one obtains with liquid or solid films or plates formed from them must necessarily be made up of groups of wave-lengths that one should be able to show are connected in a determinate way with the resonance wave-lengths of the inert gases used in making up such films or plates.

In what follows an account is given of an investigation we recently initiated on the absorption of light by gaseous, liquid, and solid xenon,* one of the rare gases that has only recently become available in considerable quantities.

4. Xenon and its use in Absorption Experiments.

In Table I there is collected the resonance wave-lengths of the inert gases, their frequencies and certain critical data required for reference.

Table I.

Inert gases--Data.				Critical temperature (° C.).	Critical pressure (atmo- spheres).
Element.	At. No.	Resonance lines.			
		$h\nu_1=^1S_0-^1P_1.$	$h\nu_2=^1S_0-^3P_1.$		
Neon	10	736	744	-210	—
Argon.....	18	1048	1066	-117.4	52.9
Krypton.....	36	1165	1236	- 62.5	54.3
Xenon	54	1293	1469	14.7	57.2
Niton	86	1452	1786	104.5	62.0

From these data it will be seen that all of the resonance wave-lengths fall below the spectral region one covers by the use of a quartz-spectrograph and

* When this paper was communicated to the Royal Society our attention was drawn to a paper on the absorption of light by xenon that we regret to say we had overlooked. In this paper, by Dr. Cuthbertson, an account was given of some very interesting experiments with xenon in a vacuum spectrograph in which he found that with the gas at a pressure of 0.5 mm., there was complete absorption up to λ 1036. Without the xenon present his spectrum—a carbon one—extended down to λ 459. From an examination of Dr. Cuthbertson's plates it occurs to us that the absorption he observed was connected with some radiation frequency characteristic of his absorbing gas and corresponding to a wave-length in the neighbourhood of λ 800. His spectrum on the long wave side, it should be mentioned, did not extend beyond λ 1277, and between λ 1036 and λ 1277 his plates did not show any absorption. This is of special interest, for one would expect to find indications in this region of an absorption band corresponding to λ 1293, one of the resonance wave-lengths of xenon.

only one-half of them are within the fluorite or Schumann region (λ 1850 Å. to λ 1200 Å.). The extremely rare and radioactive gas, niton, is obviously unsuited to the purpose of our investigation and the resonance lines of krypton are too near the limit of transmission by fluorite to be useful. The wave-length λ 1469 Å. of xenon is admirably suited, however, for our studies in absorption as it falls centrally in the Schumann region. The wave-length λ 1293 Å. can also be used under certain circumstances, as will be seen later.

In carrying out our investigation the procedure followed was to enclose the gas xenon in a very small cell provided with fluorite windows, to liquefy it by compressing it in the cell and then to freeze it there. While the xenon was in each of the three states light of suitable wave-lengths was sent through the cell, and the wave-length limits of the absorption that took place were determined by the use of a fluorite spectrograph.

5. Apparatus.

The Fluorite Spectrograph.—In our use of the fluorite spectrograph the slit, collimator and lenses were set in permanent adjustment within a specially constructed tinned brass vessel equipped with a well-fitted airtight lid. The fluorite prism was adjusted for minimum deviation of the wave-length $\lambda = 1500$ Å., and the plate holder was provided with scales that enabled one to focus at will any part of the fluorite spectral region. Schumann plates were used for taking the spectrograms. The axis of the collimator was coincident with that of a hollow tapered brass cone affixed at one end of the brass containing vessel. On this cone, which was tapered at one degree, the absorption chamber and that containing the source of light were fitted with greased tapered connections. The optical path was therefore along the common axes of the tapered connections and the collimator of the spectrograph. The vessel containing the optical parts of the spectrograph could be highly evacuated with suitable pumps and filled when necessary with pure hydrogen which, it is well known, does not absorb light in the Schumann region. Openings behind the plate holder and the hollow cone through which the collimator was pointed served respectively as inlet and outlet for the hydrogen. The latter was purified by passing it through palladiumised asbestos heated to 300° C. over phosphorus pentoxide and then through a liquid air trap. During the exposures the hydrogen was kept flowing into the spectrograph through the opening behind the plate holder and out again by the collimator tube. This prevented any dust from the spark source from being carried into the spectrograph and

deposited on its slit. The lid of the spectrograph and all the tapered connections were made vacuum tight with a resin-vaseline compound.

The Light Source.—The background spectrum chosen for the absorption was that of the light from a condensed spark between gold electrodes in an atmosphere of hydrogen. A 3 mm. spark and an inductance of 60 2-inch diameter turns of copper wire were placed in series with the gold spark. This type of excitation brought out arc and spark lines of gold as well as a continuous and many lined spectrum of hydrogen. The spectrum produced and shown as a comparison on all plates was admirably suited for work in the region λ 1400 Å. to λ 1700 Å. Wave-lengths were identified by comparison with an ordinary spark spectrum of gold in hydrogen, the wave-lengths of which were taken from the work of Bloch.*

The spark chamber was of brass and enclosed in a cooling water jacket. The electrode holders placed diametrically opposite each other were insulated from the body of the chamber by supporting tubes of pyrex glass. These glass to brass joints were tapered in towards the inside of the spark chamber and were made vacuum tight with the resin-vaseline mixture. The electrodes were screwed on the holders, and by means of the eccentric position of the screws, could be adjusted for lining up by a rotation of the holders. A water jacket about the chamber served to prevent excessive heating of the electrodes.

The Absorption Cells.—Two types of cell for holding the absorbing medium were necessary. One was adapted for working with pressure below 1 atmosphere while the other could be used for higher pressures such as those approaching the critical pressure of the gas. In each case the cell was constructed of brass with fluorite windows placed in the optical path.

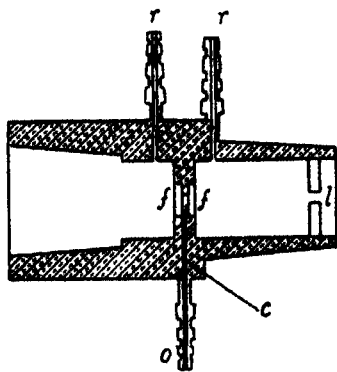


FIG. 3.

The low pressure cell is shown in fig. 3. The fluorite plates (*f*) were waxed in the recesses shown and spaced 2 mm. apart. The tubes (*r*) could be connected to allow the hydrogen flowing through the spectrograph to reach the spark chamber. In the

use of this cell care had to be taken to avoid a greater pressure within the cell than in the spectrograph and spark chamber. The cell could be

* 'J. Physique,' vol. 6, pp. 105, 154.

completely evacuated through (o) and (c) and the xenon admitted from its reservoir. The pressure in the cell could be observed on a barometer and any trace of impurities in the xenon was detected by observing the spectrum of the light from a small discharge tube. The barometer and discharge tube were both connected to the glass tube that led from the xenon reservoir to the cell. A connection could also be made through a stopcock from this system to the vacuum pumps. The xenon reservoir was made of pyrex glass and was mounted so that it could be immersed in liquid air. The xenon was purified while frozen in the reservoir by pumping off any excess of air or other non-condensable gas. As the melting point of xenon, it will be realised, is -140°C . and its boiling point -109°C .^{*} the immersion of the reservoir in liquid air enabled one to recover all the xenon at the end of an experiment.

For the experiments with high pressure an entirely different and more elaborate type of absorption cell was required. Fig. 4 shows the side and end

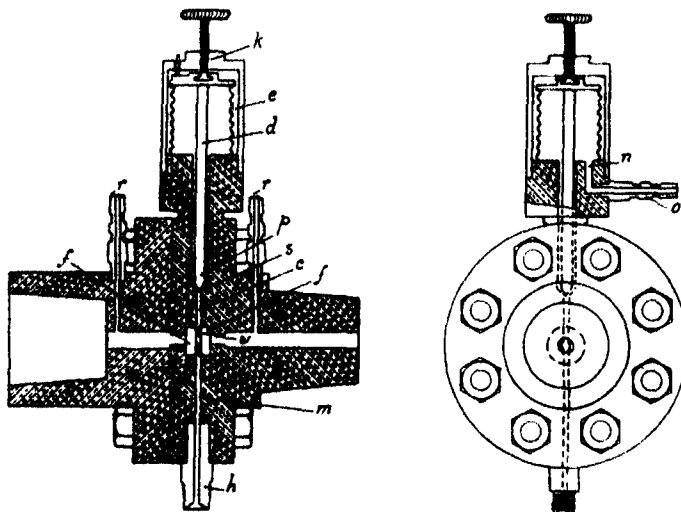


FIG. 4.

elevation of the cell employed. The fluorite windows (f) were 3 mm. thick and were waxed into their recesses. The main part of the cell consisted of two brass blocks (a) and (b) fitted with the required tapered connections for attachment (a) to the spectrograph and (b) to the spark chamber. These blocks were bolted together and with a lead washer (g) between them resting on corrugated surfaces. The fluorite plates were spaced 2 mm. apart as in

^{*} Kaye and Laby, 'Physical and Chemical Constants.'

the low pressure cell. Between the plates there was placed a small brass washer (*w*) for the purpose of reducing the volume of the cell. This washer had openings through it which connected the passages (*m*) and (*c*) with the cell. The holes (*m*) and (*c*) were made 2 mm. in diameter to allow a fair passage for the gas and also to reduce the volume. The cell could be connected with the high-pressure apparatus (fig. 5) by a coupling between (*h*)

and a nipple (*g*). The volume of the cell and the two passages (*m*) and (*c*) was about one-third of a cubic centimetre.

The volume of xenon at atmospheric pressure in the reservoir was 200 c.c. This gave about 0.60 c.c. of liquid at 0° C. and this was sufficient to prevent the mercury which was used to compress the xenon from entering the cell. In this way the cell could be adapted for the study of the liquid xenon at temperatures at or below the critical temperature (14.7° C.). The minimum volume of the liquid obtainable from the xenon used was about 0.33 c.c. at -140° C. The compressed gas was held by the needle valve (*d*) mounted on the block (*b*) that led to the xenon reservoir. This valve was of the packless type having a stainless steel spindle (*d*) supported by a phosphor-

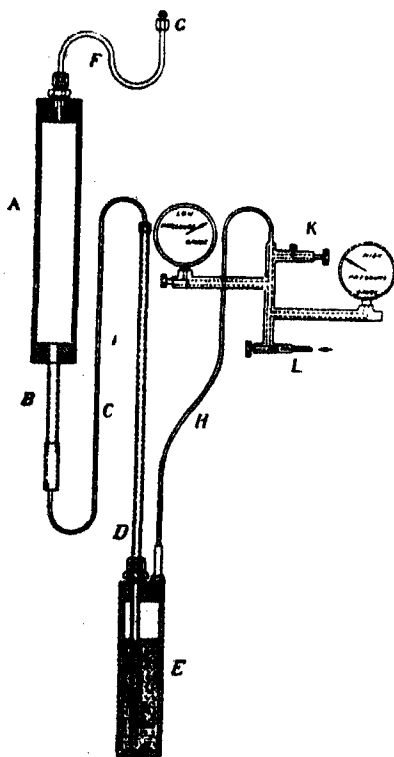


FIG. 5.

bronze bellows (*e*). The spindle could be raised or lowered by turning the screw (*k*). The height of the top of the bellows could be determined by the position of a small rod projecting through the top of the brass cap enclosing the bellows which was soldered in its position as shown in the diagram. With this form of valve the space to either side of the valve seat (*s*) was made absolutely vacuum tight. The gas from the reservoir entered the bellows first through (*o*) and (*n*). It then passed down along the valve spindle and past the valve seat into the cell. By having this direct path through the bellows any pocketing of gaseous impurities was avoided.

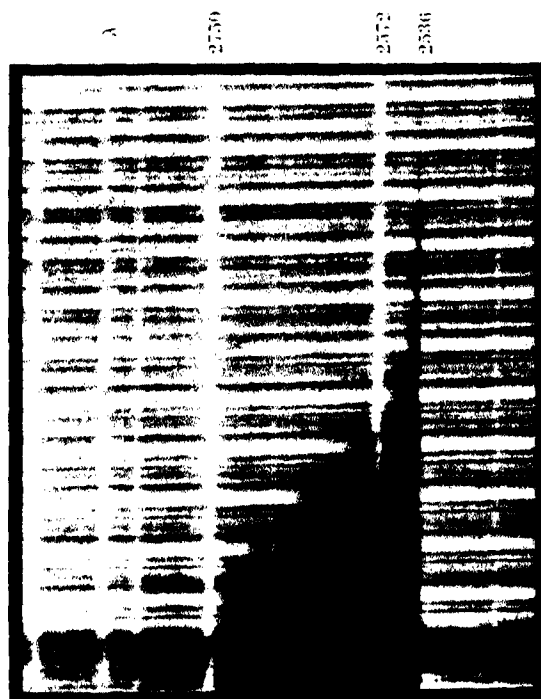


FIG. 1.

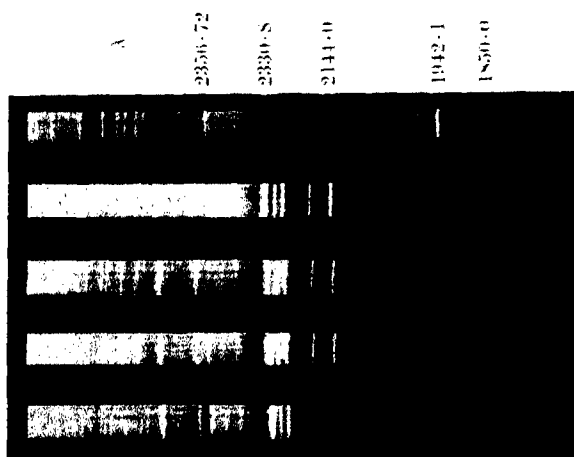


FIG. 2.

(Facing p. 274.)

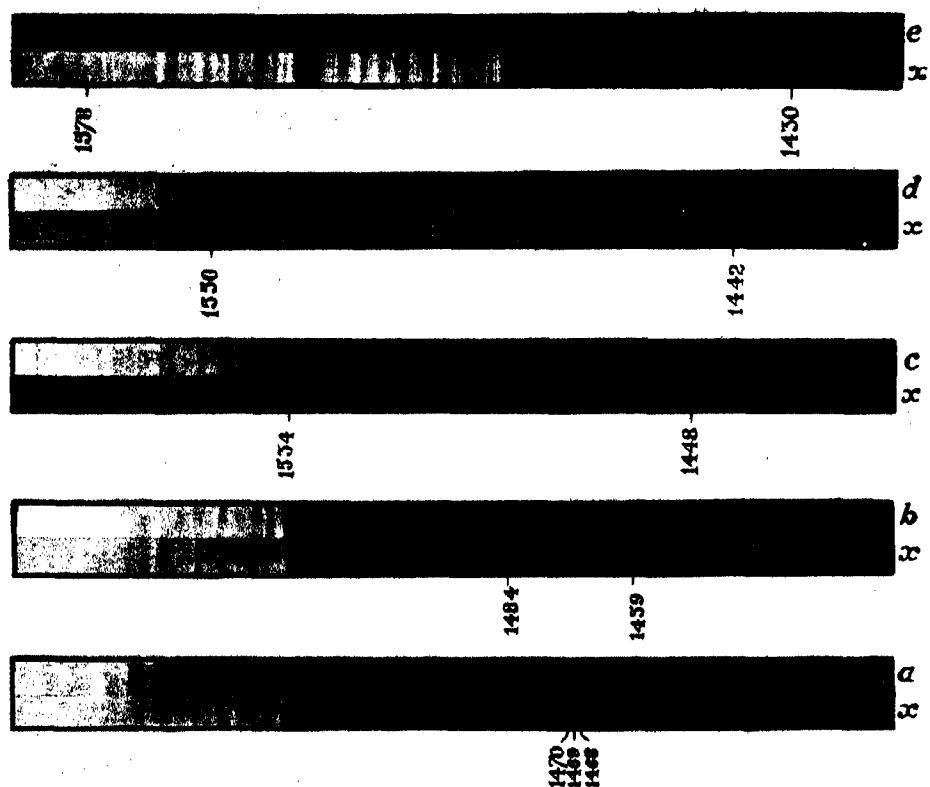


FIG. 6.

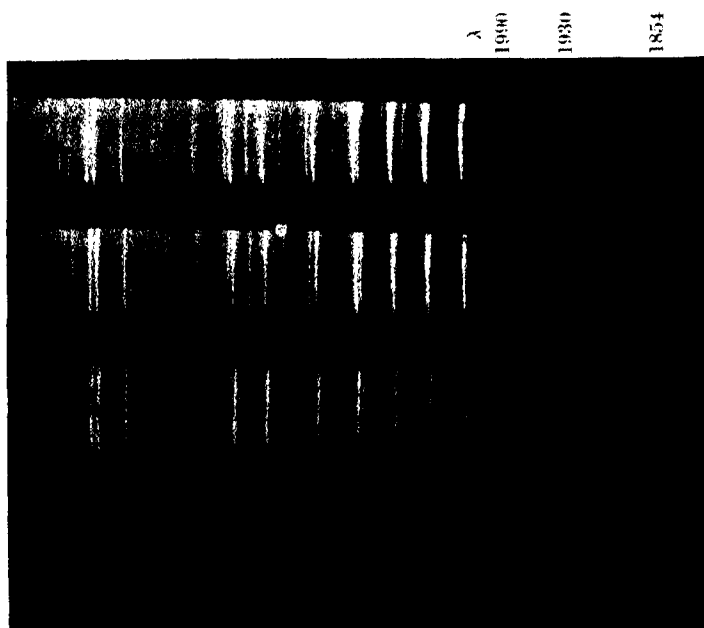
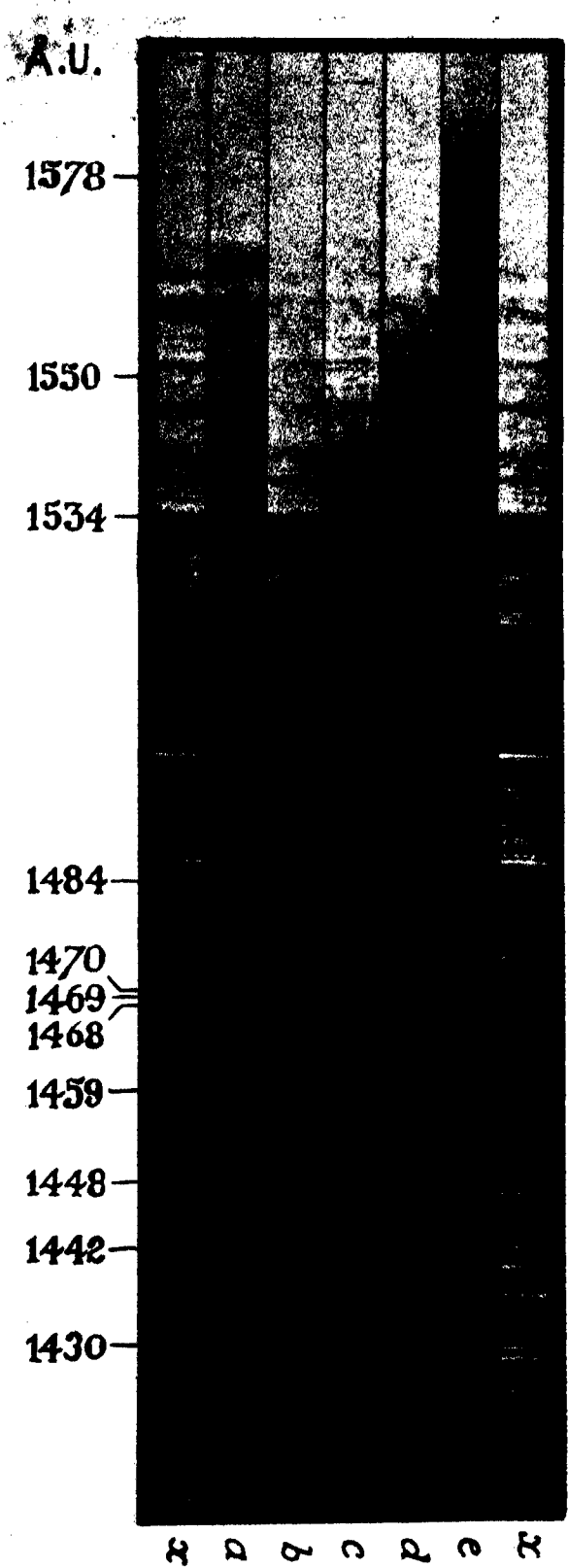


FIG. 11.



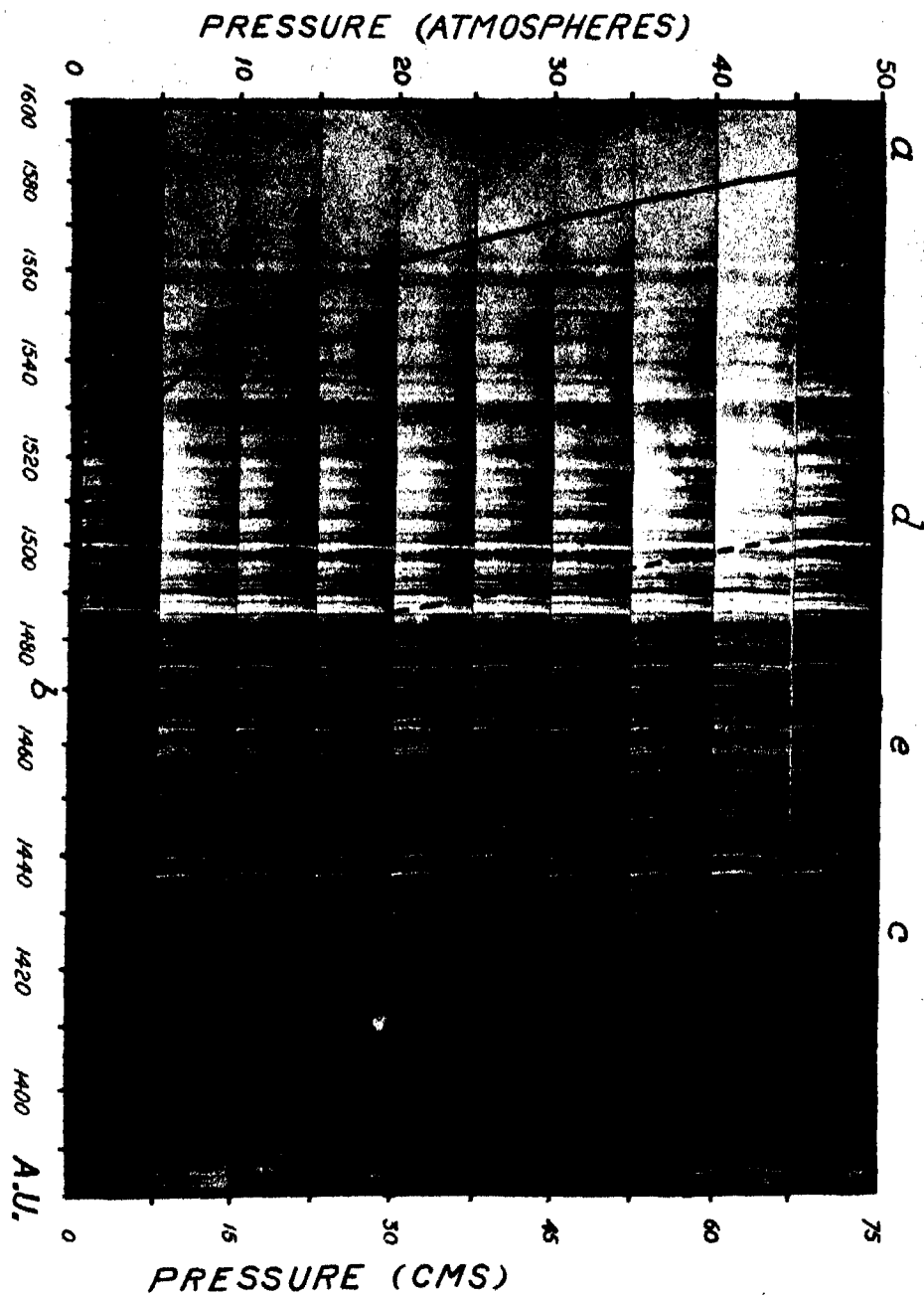


FIG. 8.

The tubes (r) corresponded to those in the low pressure cell and allowed for the flow of hydrogen from the spectrograph to the spark chamber.

The Compression Apparatus.—The method of applying the pressure to the xenon consisted in compressing it with mercury with the latter subjected to the pressure of oxygen from a high pressure cylinder. The essential features of this apparatus are shown in fig. 5. The compression chamber (A) was of 3-inch medium steel pipe, plugged and iron welded at each end. Its capacity was about 300 c.c. The mercury reservoir (E) was made of heavier steel pipe $3\frac{1}{2}$ inches in diameter and similarly welded. The volume of mercury kept in the reservoir was 450 c.c. The compression chamber was connected by a 2-mm. capillary tube with suitable couplings to (h), fig. 4, beneath the pressure cell. A short piece of $\frac{3}{4}$ -inch drawn steel tubing (B) led from the compression chamber and was joined to a steel capillary tube (C) forming a U-tube with the latter. This capillary, which was three-sixteenths of an inch in diameter, rose to a height of 22 inches and was then bent down to join a straight piece of $\frac{1}{2}$ -inch steel tubing (D) that led down into the reservoir (E). The tube (D) extended above the level of the mercury in the reservoir (E) to a distance greater than barometric height and its lower end was about $\frac{1}{4}$ inch from the bottom of the mercury reservoir. From the reservoir (E) connection was made by means of a copper tube (H) to pressure gauges and valves for applying and releasing the pressure on the mercury. The actual pressure on the gas in the compression cell was taken from a gauge reading corrected for the estimated height of the mercury in the system.

This type of compressor had the great advantage that it had no complicating valves between the mercury reservoir and the absorption cell. Also the U-tube formed by the tubes (B) and (C) when immersed in liquid air served as a place in which to freeze the xenon over from the gas reservoir. At the end of an experiment the mercury could be syphoned back into the reservoir (E).

6. *Experimental Procedure with High Pressure.*

The cycle of operations for determining the absorption at a high pressure was as follows.

A photographic plate was placed in the spectrograph and the lid replaced. To avoid the presence of moisture a small dish filled with phosphorus pentoxide was left in the spectrograph. With the aid of a Cenco Megavac pump and mercury diffusion pump with a liquid air trap the spectrograph and spark chamber were evacuated. With this vacuum retained the pressure cell and compressor were evacuated next. The release valve (K) was kept open and

the mercury rose in the tube (D) to barometric height. When this system was completely exhausted as indicated by the discharge tube in the line, the connection to the pumps was closed. The xenon was then allowed to flow into the cell and compressor and frozen in the U-tube (BC).

The needle valve on the cell was then closed and the U-tube allowed to warm up. The xenon filled the compression chamber and cell at a pressure of two-thirds of an atmosphere. The release valve (K) was closed and oxygen from the high pressure cylinder was admitted through (L) to the mercury reservoir with the result that the mercury was forced up into the compression chamber (A). The pressure on the xenon was built up slowly to the value required and then the oxygen supply was cut off.

With the xenon at the pressure required the spectrograph and spark chamber were filled with hydrogen which was allowed to flow slowly from the spectrograph past the spark and then to the outside air.

For a suitable photograph an exposure of 2 hours was necessary.

At the end of an exposure the spectrograph and the spark chamber were again evacuated. By opening the release valve (K) the pressure on the xenon was reduced to two-thirds of an atmosphere. After this the bellows valve was opened and the xenon was frozen back into the pyrex reservoir. Hydrogen was admitted to the cell and compressor and allowed to fill this system to a pressure of 1 atmosphere. This caused the mercury remaining in the chamber (A) to be syphoned back through the capillary (C) into the lower reservoir. In this way the U-tube (BC) was freed of mercury and so the experiment could be repeated.

7. Results of Experiments with Gaseous Xenon.

The experiments on absorption by gaseous xenon were carried out in the winter season, and the room in which the observations were made was kept at a temperature of 12° C. by allowing a suitably regulated stream of air from outside the building to circulate about the room. The observations showed that with the gas in the compressure cell at a pressure of 2 mm. of mercury the absorption appeared on the spectrogram as a line at λ 1469 Å. As the pressure of the xenon was increased the absorption rapidly widened out into a band and at 50 atmospheres it had a width of 156 Å. Table II gives the wave-length limits of the absorption band for various pressures.

Table II.—Limits of Absorption Band for Wave-length $\lambda = 1469 \text{ \AA}$.

Pressure.	Limit long wave- length side.	cm. ⁻¹ .	$\Delta\nu$ cm. ⁻¹ .	Limit short wave- length side.	cm. ⁻¹ .	$\Delta\nu$ cm. ⁻¹ .	Centre of band. cm. ⁻¹ .
	$\text{\AA}$.			$\text{\AA}$.			
2 mm.	1469	68070		1469	68070		
1 cm.	1470			1468			
5 "	1472			1468			
10 "	1475			1467			
20 "	1482			1463			
30 "	1487			1459			
40 "	1490			1458			
1 atmos.	1507	68400	1670	1456	68540	470	67470
2 "	1518	65800	2270	1454	68760	690	67280
5 "	1534	65040	3030	1448	69060	990	67050
10 "	1550	64560	3410	1442	69340	1270	66950
20 "	1562	64040	4030	1439	69560	1490	66800
30 "	1574	63580	4490	1436	69700	1630	66640
40 "	1578	63240	4830	1430	69960	1890	66600
50 "	1584	63020	5050	1428	70120	2050	66570

In the table $\Delta\nu$ gives the shifts of the limits of the absorption band from the main frequency 68070 cm.^{-1} ($\lambda = 1469 \text{ \AA.U.}$). The outstanding features of the absorption it will be seen are the unilateral spread towards the longer wave-lengths and the rapid onset of the broadening with pressure increase.

Figs. 6 and 7 (Plates 14, 15) show the photographs of some of the absorptions.

x, comparison background spectrum.

a, absorption at 1 cm.

b, " 30 cm.

c, " 380 cm. (5 atmospheres).

d, " 760 cm. (10 atmospheres).

e, " 3040 cm. (40 atmospheres).

A composite picture was made up showing how the broadening of the absorption band varied with pressure. This is shown in fig. 8 (Plate 16). The heavy continuous curve *abc* indicates the position of the edges of the absorption band. The branch (*a*, *b*) denotes the long wave-length limit and (*b*, *c*) the short wave one. The dotted curve shows how the absorption broadened with pressures up to 75 cm.

Fig. 9 shows a curve for the high pressure absorption limits plotted with

pressures in atmospheres as ordinates and the positions of the corresponding absorption limits as abscissæ expressed in wave-numbers as frequency units.

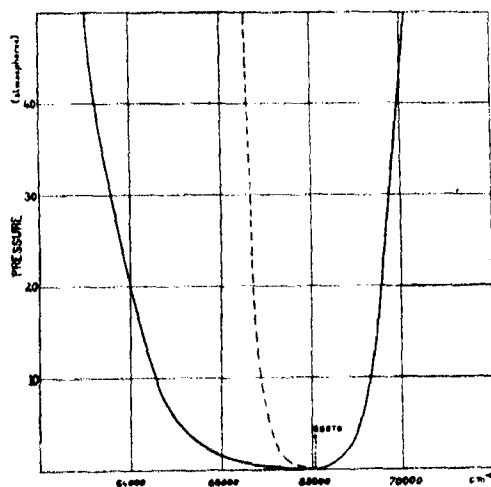


FIG. 9.

The dotted curve shows how the centre of the band was shifted towards the long wave-length side.

8. Results of Preliminary Experiments with Liquid and Solid Xenon.

In regard to the absorption by liquid and solid xenon, we are able to present but a preliminary report. Unexpected experimental difficulties were encountered, but these are being overcome gradually. Our first absorption spectrogram taken with liquid xenon, which is a clear and colourless liquid, was obtained when working with the room and apparatus at a temperature of 8° C. The pressure used in liquefying the gas was 50 atmospheres and the compression cell was the one shown in fig. 4. The plate holder of the spectrograph was set to photograph the spectral region below λ 1700 Å. A 2 hours' exposure gave no trace of a spectrum. This went to show that the width of the absorption band was considerably greater than that of the band obtained with a gas pressure of 50 atmospheres.

One of the difficulties experienced at this stage arose from the formation of a fine powder in the absorption cell whenever the liquid xenon came into contact with the wax that was used to seal in the fluorite plates used as sides to the absorption cell. To get over the formation of this powder it was decided to proceed on new lines and to endeavour for the present to determine the limit

on the long wave side of the absorption band obtainable with liquid and solid xenon. In doing this we used an absorption cell which we constructed out of thin walled fused quartz. This cell and the chamber in which it was enclosed are shown in fig. 10. The cell was cooled by a blast of cold gaseous nitrogen

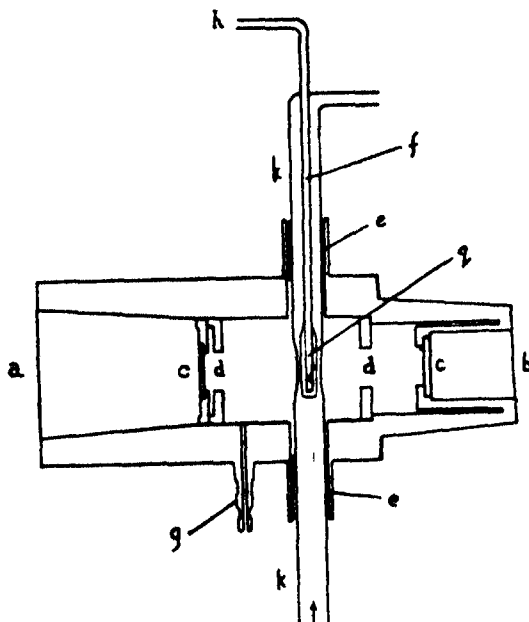


FIG. 10.

or hydrogen and the xenon was readily liquefied or solidified at will by regulating the temperature of the gas stream. The cell is shown and designated as (*q*) in fig. 10. The blast of gas that cooled this cell was led past it by the tube (*k*). The xenon itself was admitted to the cell through a tube (*h*). The two quartz windows (*c*) were waxed into the mounting (*a*, *b*) so that the space between them and the cell could be evacuated to prevent frosting of the surface of the tube (*k*). This latter was supported tightly in position by two rubber washers (*e*) and was also waxed in place in the mounting and firmly bound with tape as well to give it rigidity. Diaphragms (*d*) were inserted in the mounting to prevent light from the sides of the tube (*k*) reaching the slit of the spectrograph. The openings in these diaphragms were rectangular and had a width of only 3 mm. The cell mounting was made with tapered ends so that it could be readily attached at (*a*) to the spectrograph and at (*b*) to the spark chamber.

In the first experiments with this cell the source of light used was a con-

densed spark between one terminal made of aluminium and a second made up of an alloy of zinc, cadmium and lead. The space (*dd*) was highly evacuated and liquid xenon and solid xenon were in turn formed in the cell (*g*). Solid xenon was clear and colourless glass-like substance. Light was sent through the cell and spectrograms were taken with a quartz spectrograph. These showed that both the liquid and solid xenon did not absorb radiation of wave-length longer than $\lambda = 1990 \text{ \AA}$. Between $\lambda 1990 \text{ \AA}$. and $\lambda 1854 \text{ \AA}$. there was partial absorption. Reproductions of the spectrograms taken are shown in fig. 11 (Plate 14). The spectrum (*a*) was obtained with the cell empty and at room temperature (*b*) when the cell was empty but cooled by the stream of cold gas through (*k*). The spectrum (*c*) was obtained with liquid xenon in the cell and (*d*) with solid xenon in it. In the originals of (*c*) and (*d*) the group of wave-lengths near $\lambda 1854 \text{ \AA}$. could be quite readily seen.

In a second experiment gold electrodes were used in the spark chamber and an exposure was made with the fluorite spectrograph. Both the spectrograph and the spark chamber were kept filled with pure hydrogen and the chamber (*dd*) above the cell was kept evacuated. With the cell empty but cooled with a blast of cold hydrogen gas through the tube (*k*), lines in the gold spectrum were obtained down to $\lambda 1760 \text{ \AA}$. With the cell filled with liquid xenon at 80 cm. pressure no lines were obtained below $\lambda 1783 \text{ \AA}$. From this result one can conclude that on the long wave side the limit of the absorption band produced by liquid xenon at atmospheric pressure, and therefore approximately at the temperature -110° C ., is $\lambda 1783 \text{ \AA}$. For solid xenon the corresponding limit is likely to be found to be about $\lambda 1800 \text{ \AA}$. It would have been interesting to obtain the limit of the absorption bands of both liquid and solid xenon on the short wave-length side as well, but, with the time available for our co-operation coming to an end, this was not possible. We hope to deal with this matter in a later communication, and we shall also endeavour to obtain some information about the absorption band corresponding to $\lambda 1293 \text{ \AA}$. obtainable with gaseous liquid and solid xenon. In this part of the investigation we expect to use a specially constructed cell with fluorite sides in combination with a vacuum grating spectrograph.

9. Discussion of Results.

In the type of absorption we have obtained with xenon, and in that pointed out in the earlier part of this paper as obtained with mercury vapour in the neighbourhood of $\lambda 2536.72 \text{ \AA}$., we have similar effects. In both cases the absorption band develops asymmetrically on the long wave side. In the one

case the absorptive medium was a monatomic gas and on the other a monatomic vapour. With the mercury vapour the broadening was, if anything, more asymmetrical than with xenon. In both cases the absorption band developed about a resonance spectral line that originated in an electronic transition from a singlet to a triplet energy level $h\nu_1 = {}^1S_0 - {}^3P_1$ of the atoms involved. It is not clear as yet what this asymmetry in the absorption signifies, but it may be connected with the deeper atomic energy level having a single multiplicity and with the upper one having a triplet one. It would be interesting to see if some type of asymmetry were a characteristic feature of the Stark effect or of the Zeeman effect one obtains with a wave-length whose frequency is given by $h\nu_1 = {}^1S_0 - {}^3P_1$. With mercury vapour the evidence we have available indicates that the absorption band one develops in connection with the spectral line $\lambda = 1849.6 \text{ \AA.}$ is symmetrical in form. In this case it may be noted the atomic energy levels involved are single for $\lambda = 1849.6 \text{ \AA.}$ is given by $h\nu_2 = {}^1S_0 - {}^1P_1$. Possibly the wave-length $\lambda = 1849.6 \text{ \AA.}$ will show symmetrical Stark and Zeeman effects in contradistinction to those of the wave-length $\lambda 2536.72 \text{ \AA.}$

It is of interest to recall here that approximate limits at or near $\lambda 1800 \text{ \AA.}$ were obtained for the long wave side of the absorption bands given by liquid and solid xenon. If this additional widening of the absorption band that followed upon the liquefaction and solidification of xenon were entirely an effect resulting from an increase in pressure, one would have in this absorption by xenon a means of estimating the so-called "intrinsic pressure" for a liquid, and in particular for liquid xenon. It would suffice for the purpose to extrapolate to $\lambda 1800 \text{ \AA.}$ the long wave side of the full line curve (*a, b, c*) shown in fig. 8. It is clear this would lead to very high pressures, but the rise of the curve (*ab*) for pressures above 50 atmospheres is not sufficiently definable for us to assign at present any very reliable value to the intrinsic pressure.

From the experimental results obtained in our investigation and described in this paper some general conclusions can be drawn as to the significance of the broadening of the absorption band observed. Associated with each atom in the gas there must be an energy distribution function. This is seen to vary in a remarkable way with pressure. The energies of the atoms depend on their mutual influence and this varies with pressure and temperature. Collisions and interaction of the electromagnetic fields of the atoms during temporary grouping would account for a change of atomic energies. Occurrences of this nature would of necessity show an important working of the well-known Zeeman and Stark effects. These factors are negligible in the case of a gas in

a rarefied state, and with a gas in this state we can have only two unique energy levels involved. This necessarily leads directly to transitions that can give only line absorption.

Our investigation does not reveal the form of the energy function any further than showing the effect of its change with pressure on the absorption. The function for any level will, no doubt, be of a probability type. The absorption band represents the transitions from any of the sublevels of the lower state to any one in the upper state. Intensity of absorption in the band for a particular frequency would therefore depend on the numbers of atoms in the interchanging states and perhaps a probability law governing transitions between sublevels of upper and lower states.

The width of the absorption band has been shown to be asymmetrical with pressure for the singlet triplet transition. That is, the energy functions for the singlet and triplet levels appear to be fundamentally different. It is of vital importance therefore to investigate the singlet to singlet absorption band corresponding to $h\nu_2 = {}^1S_0 - {}^1P_1$. If the form of the function changes only with multiplicity we should expect an absorption symmetrical with pressure. Work on the absorption band corresponding to the lower resonance wavelength of xenon ($\lambda = 1293 \text{ \AA.}$) is therefore to be carried out.

The simplicity of the xenon atom and other factors connected with its liquefaction and solidification as well as with the wave-lengths of its resonance lines mark it out as a unique element with which to work in developing the spectroscopy of liquids and solids.

[*Note added August 6, 1930.*—Since the communication given above was made to the Royal Society, we have carried out additional experiments on the absorption of light by liquid xenon at a set of different temperatures. The cell shown in fig. 4 was used with the fluorite plates replaced by others of fused quartz 2 mm. in thickness. These were cemented in place with red sealing wax which was found to resist the disintegrating action previously experienced of liquid xenon under pressure. Arrangements were made for cooling the whole cell to the selected low temperatures by the use of a blast of air cooled with liquid air and suitably regulated in flow. The empty cell was found to transmit radiation down to $\lambda 1600 \text{ \AA.}$, but a quartz spectrograph sufficed to study the absorption. Absorption spectrograms were obtained with the liquid xenon in the cell at the temperatures 10° C. , 0° C. , -5° C. and -10° C. These are shown in fig. 12 (Plate 17). The absorption limits obtained in these experiments and that obtained in our earlier work are given in Table III.

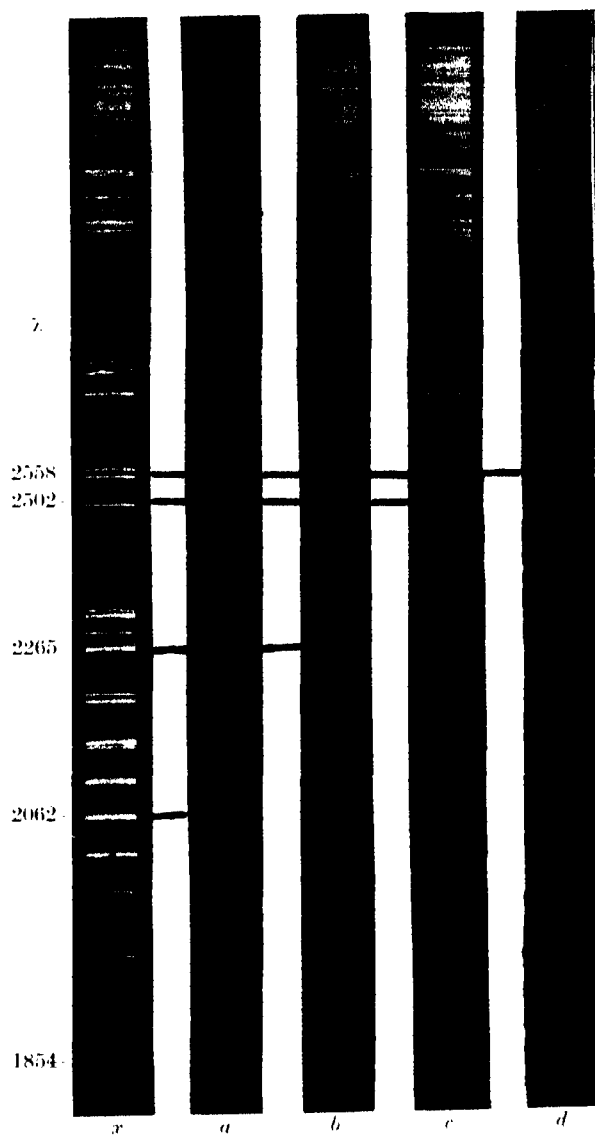


FIG. 12.

Table III.—Limits of absorption of $\lambda = 1469 \text{ \AA.}$ band.

Temperature.	Pressure.	Red Absorption Limit.
$^{\circ} \text{C.}$		
10	52 atmospheres	$\lambda = 2062 \text{ \AA.}$
0	45 "	2265 $\text{\AA.}$
-5	42 "	2502 $\text{\AA.}$
-10	38 "	2558 $\text{\AA.}$
-110	80 centimetres	1783 $\text{\AA.}$

In fig. 12 (Plate 17) "x" is a comparison spectrum of the radiation from a spark between an aluminium electrode and one of an alloy of zinc, cadmium and lead. Spectrogram "a" shows the absorption limit obtained at 10°C. , "b" at 0°C. , "c" at -5°C. , and "d" at -10°C. The remarkable result that emerged from these observations was that as liquid xenon was cooled from 10°C. to -10°C. the absorption band steadily widened out on the long wavelength side to $\lambda = 2558 \text{ \AA.}$ and then narrowed up again until at -110°C. the limit to the absorption on the long wave side was $\lambda = 1783 \text{ \AA.}$ It appears then that liquid xenon possesses a maximum optical density at some temperature between -10°C. and -110°C.

In conclusion, the authors wish to thank the National Research Council of Canada for a scholarship awarded to one of them—R. Turnbull. They are also indebted to Mr. M. F. Crawford, Mr. J. O. Wilhelm and Mr. H. J. C. Ireton for valuable assistance received from them during the investigation. To Messrs. The Adam Hilger Company they are indebted for a contribution made towards the purchase of the xenon used.

Further Investigations on the Kinetics of Gaseous Oxidation Reactions.

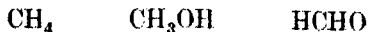
By R. FORT and C. N. HINSHELWOOD, F.R.S.

(Received June 28, 1930.)

Introduction.

Investigation of the kinetics of the oxidation of ethylene* and of benzenet† showed that these reactions are peculiar in the following respects. First, the relation between the rate of reaction and concentration is such that the reactions possess no simple "order," though the nearest integral value for the order is about the third or fourth. The rate increases very rapidly with increasing hydrocarbon concentration, but is relatively little influenced by oxygen; under some conditions oxygen may have a retarding influence. Secondly, the reactions can be slowed down by increasing the surface exposed to the gases. This indicates that the oxidation occurs by a chain mechanism. Thirdly, the rate of change of pressure accompanying the oxidation only attains its full value after an induction period, during which evidently intermediate products are accumulating.

Accepting the fact that the oxidations are probably chain reactions, the relation between rate and concentration shows that the chains are much more easily propagated when the intermediate active molecules encounter more hydrocarbon than when they encounter oxygen. Following the view of Egerton,‡ and consistently with previous work on the combination of hydrogen and oxygen,§ the working hypothesis adopted is that some intermediate peroxidised substance is responsible for the propagation of the chains. This being so, the question arises whether the peculiarities found in the oxidation of hydrocarbons will also be found with substances already containing oxygen. To investigate, therefore, the influence of chemical configuration on the mechanism of oxidation reactions the following series of compounds|| has been studied



* Thompson and Hinshelwood, 'Proc. Roy. Soc.,' A, vol. 125, p. 277 (1929).

† Fort and Hinshelwood, 'Proc. Roy. Soc.,' vol. 127, p. 218 (1930).

‡ Egerton and Gates, 'J. Inst. Petroleum Technol.,' vol. 13, p. 281 (1927).

§ Thompson and Hinshelwood, 'Proc. Roy. Soc.,' A, vol. 122, p. 610 (1929).

|| Methane not in very great detail. We believe the problem of methane is also being studied elsewhere.

which represent the stages through which Bone and others have shown the oxidation of methane to occur.

It may be stated at the outset that the oxidations not merely of methane, but equally that of methyl alcohol and formaldehyde show the characteristics described above. Thus the first product of interaction of a hydrocarbon and oxygen is by no means the only one which can give rise to chains. Their propagation appears to be conditioned more by the energy available than by the exact chemical configuration of the molecules.

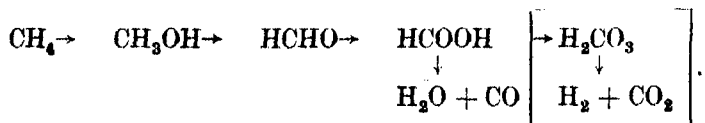
As will be seen, the kinetic relationships to which the chain mechanism gives rise are very complicated. But an approximate quantitative treatment of the typical example of methyl alcohol will be given in a later section.

Experimental Method.

The method of investigation was the same as that described in previous papers,* the reactions being followed by observation of the pressure changes which accompany them. Methane was obtained from a cylinder of natural gas freed from hydrogen by passage over copper oxide heated to 320°-340°, and then fractionated from liquid air after removal of carbon dioxide. It still contained some nitrogen, which was, however, considered to be harmless. Methyl alcohol vapour was obtained from a sample of the liquid which had been very highly purified for conductivity measurements. Formaldehyde vapour was obtained by heating dried paraformaldehyde in a small bulb attached to the reaction vessel.

The Course of the Reactions.

The principal products of reaction are carbon monoxide and steam, even when oxygen is in excess. According to Bone's scheme† this is because the final stage is the decomposition of formic acid



Only with methane is the proportion of carbon dioxide considerable, and

* 'J. Chem. Soc.' vol. 125, p. 393 (1924); 'Proc. Roy. Soc.' A, vol. 111, p. 245 (1926); vol. 118, p. 170 (1928); vol. 127, p. 218 (1930).

† "Flame and Combustion in Gases," Bone and Townend (1927).

here it is quite possible that some direct oxidation of carbon monoxide occurs at the rather high temperature required by the reaction.

	Methane. 150 mm. CH ₄ 300 mm. O ₂ .	Methyl alcohol. 100 mm. CH ₃ OH 200 mm. O ₂ .	Formaldehyde. 200 mm. HCHO 200 mm. O ₂ .
CO ₂	Per cent. 20.2	Per cent. 7.0	Per cent. 4.8
CO	29.2	35.2	54.0
O ₂	35.6	52.3	36.9
Residue	15.0	5.5	4.3

The range of temperature in which the rate of reaction is measurable is very different for the three substances, the temperature required being greatest for methane and least for formaldehyde.

	Temperature at which half life for standard pressure is 5 minutes.	Heat of activation.
CH ₄	• 470	Calories 61,500
CH ₃ OH	442	62,500
HCHO	321	20,600

As may be seen from the equations of the chemical changes, the increase of pressure accompanying the oxidation to carbon monoxide is great enough to serve as a measure of the progress of the reactions, *e.g.*, $\text{CH}_3\text{OH} + \text{O}_2 = \text{CO} + 2\text{H}_2\text{O}$ gives an increase equal to the pressure of methyl alcohol. Owing to the fact that some carbon dioxide is formed the observed pressure increase is somewhat smaller. As long as there was enough oxygen for combustion of all the methyl alcohol to carbon monoxide the pressure increase for a given pressure of the alcohol was constant and independent of the excess of oxygen. This fact facilitates the consideration of the results from the kinetic point of view.

Pressure of methyl alcohol.	Pressure of oxygen.	Increase.	Increase Pressure of CH ₃ OH
mm. 50	mm. 250	42.5	0.85
100	250	85	0.85
150	250	130	0.87

As shown in fig. 1, when the increase of pressure is plotted against time, the curve shows an induction period, the cause of which must be primarily connected with the occurrence of the oxidation in stages. Only when a small definite amount of the intermediate product has accumulated will its rate of destruction become equal to its rate of formation, and only when this stationary condition is established will the full rate of pressure increase be observed.

As an example an experiment with methyl alcohol may be considered. At 437° with 100 mm. methyl alcohol and 200 mm. oxygen the maximum rate of pressure increase was not attained for about 100 seconds. During this time the increase of pressure was 5 mm. From a curve it could be seen that had there been no induction period, that is, had the methyl alcohol been oxidised direct to carbon monoxide, the increase during this time would have been 14 mm., and this increase would represent the disappearance of 14 mm. of methyl alcohol. We may assume that these 14 mm. of methyl alcohol were in fact oxidised during the induction period, but only to intermediate products. If all had gone to formaldehyde the increase would have been 7 mm.; the observed increase is actually slightly less even than this, but we shall probably be right as regards order of magnitude if we conclude that at the end of the induction period most of the 14 mm. of methyl alcohol have been converted into formaldehyde. The question now is whether formaldehyde vapour at such a concentration would at this temperature be oxidised as fast as it is formed, so that a stationary condition can be established. By extrapolation of the direct measurements which were made it can be calculated that formaldehyde vapour would be oxidised at the required rate of 14 mm. per 100 seconds under the conditions of this experiment if its pressure were 17 mm. This is near enough to the concentration estimated to prevail at the end of the induction period for the establishment of the stationary condition to be quite possible.

There appears to be no difficulty about interpreting the induction period in the oxidation of methane in a similar way; but there is a difficulty in the case of formaldehyde. Here it would be natural to attribute the induction period to an initial accumulation of small amounts of formic acid. But formaldehyde is oxidised to carbon monoxide and water at a temperature where direct experiment under similar conditions showed formic acid to be very stable in comparison with what might have been expected. Thus the course of the oxidation must be somewhat more complex than the formulæ given at the beginning of this section indicate. While the scheme given there undoubtedly expresses the general behaviour correctly, other intermediate peroxidised substances probably play their part also.

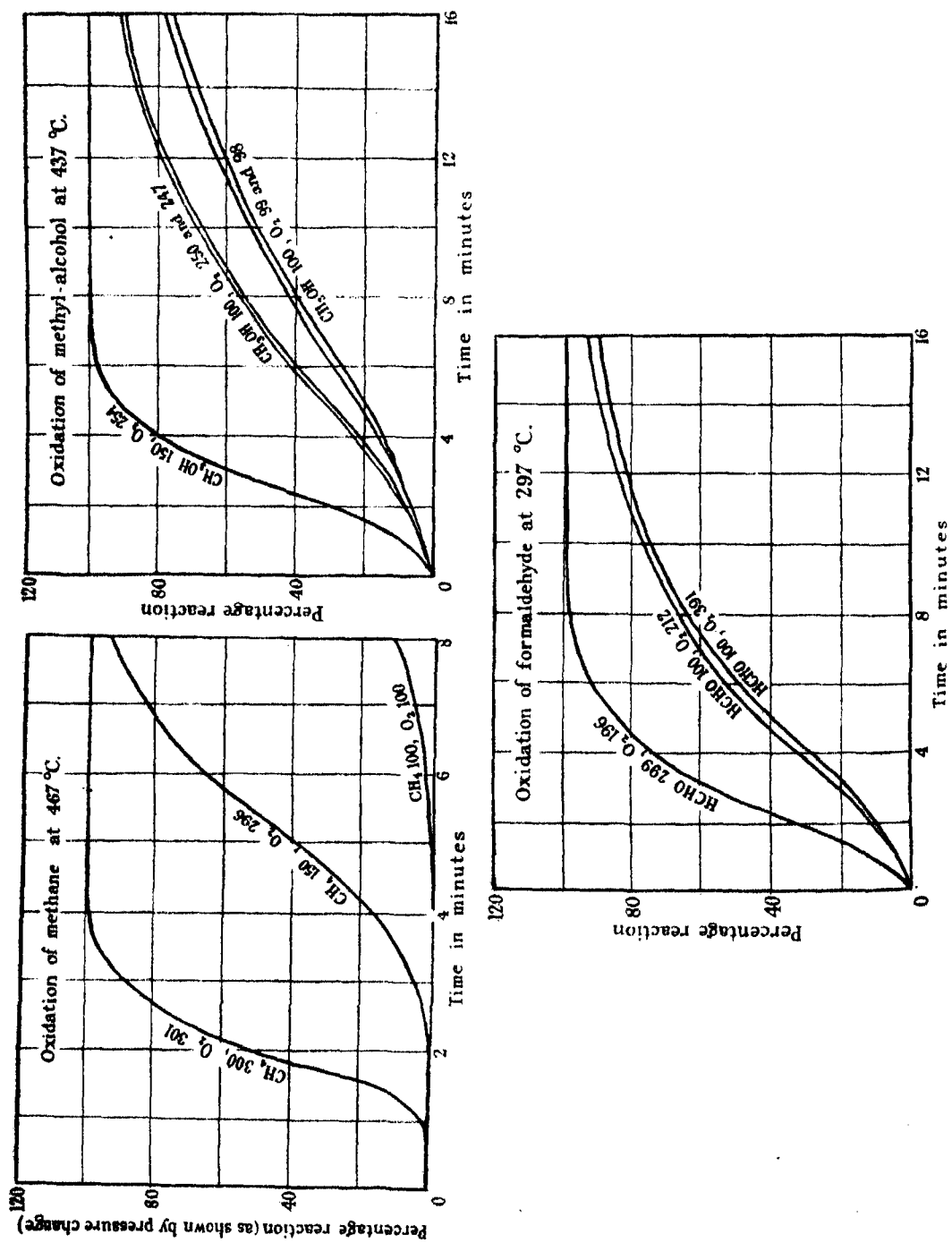


FIG. 1.

Some typical experiments, from which the curves in fig. 1 are taken, are recorded below. t is the time, x is the percentage of the total pressure increase which has occurred.

Methane 467° C.

99 mm. CH ₄ . 202 mm. O ₂ . Total pressure increase 21 mm.		150 mm. CH ₄ . 296 mm. O ₂ . Total pressure increase 34 mm.		300 mm. CH ₄ . 301 mm. O ₂ . Total pressure increase 59 mm.	
t .	x .	t .	x .	t .	x .
' "		' "		' "	
6 58	5	3 6	6	1 1	2
7 52	10	3 53	15	1 16	7
9 26	19	4 22	23	1 34	19
11 16	33	4 52	35	1 45	31
12 35	52	5 14	44	1 55	42
16 10	67	5 33	53	2 6	56
19 40	85	6 0	65	2 21	71
		6 27	74	2 39	83
		6 58	82	2 58	88
		7 43	91	3 30	97
		8 31	97		

Methyl Alcohol 437° C.

100 mm. CH ₃ OH 99 mm. O ₂ . Total pressure increase 86 mm.		100 mm. CH ₃ OH 250 mm. O ₂ . Total pressure increase 84 mm.		150 mm. CH ₃ OH 254 mm. O ₂ . Total pressure increase 130 mm.	
t .	x .	t .	x .	t .	x .
' "		' "		' "	
1 36	3.5	1 32	4	0 36	3
2 24	7	2 15	8	1 0	7
3 23	13	3 45	20	1 26	14
5 8	24	4 22	26	1 53	26
6 53	36	6 18	44	2 33	41
8 46	48	7 46	56	2 55	57
11 5	60	9 35	68	3 13	64
14 6	72	11 57	80	3 34	72
16 19	81	13 53	86	4 4	80
21 24	91	17 31	95	5 5	91
23 33	94			6 51	98

Formaldehyde 297° C.

100 mm. HCHO. 212 mm. O ₂ . Total pressure increase 41 mm.		100 mm. HCHO. 391 mm. O ₂ . Total pressure increase 40 mm.		299 mm. HCHO. 196 mm. O ₂ . Total pressure increase 111 mm.	
<i>t.</i>	<i>x.</i>	<i>t.</i>	<i>x.</i>	<i>t.</i>	<i>x.</i>
1 2	4.5	1 25	5.5	0 27	3
2 6	12	2 5	10.5	0 44	7
2 57	20	3 14	21.5	1 14	16
4 9	34	4 29	35	1 39	25
5 33	49	5 38	46	2 2	35
7 8	63	6 32	54	2 47	53
8 12	71	7 41	65	3 13	62
11 49	85	10 47	78	4 29	80
17 13	95	18 42	95	6 16	94

Influence of Concentrations on the Rate of Reaction.

The analysis of the kinetics of these reactions is complicated by the existence of the induction period. We may, however, assume that when once the maximum rate of pressure increase is established it will measure the actual rate of oxidation of the initial substance, methane, methyl alcohol or formaldehyde as the case may be, since any intermediate products will be disappearing at the same rate as they are formed. Consequently in dealing with the kinetics of the various oxidations we have attached significance only to those parts of the curve which represent the reaction after the induction period. The method of recording the results depends upon the fact that, after the induction period is over, the ratio of the times required for any given fraction of the reaction at two pressures is approximately the same, whatever the actual fraction chosen may be. This is illustrated by the following table.

Initial pressure of		Relative times.				
CH ₃ OH.	O ₂ .	0-10 per cent.	10-20 per cent.	20-40 per cent.	40-60 per cent.	60-80 per cent.
150	250	1	1	1	1	1
50	250	4.8	9.5	10.3	10.4	12.4
		4.4	9.5	9.4	10.6	11.9

Since the ratio of the times for each of the intervals after the first is approximately the same, the average values for the range 20 to 80 per cent. may be used for the purpose of expressing the influence of any desired factor on the rate of reaction. This method of representation is adopted in all the following tables.

Methane 487°.		Methyl alcohol 437°.		Formaldehyde 297°.	
(a) Oxygen pressure constant at 300 mm.		(a) Oxygen pressure constant at 250 mm.		(a) Oxygen pressure constant at 200 mm.	
Initial pressure of CH ₄ .	Relative values of reciprocal of time for reaction to go from 20-80 per cent.	Initial pressure of CH ₃ OH.	Relative reciprocal time.	Initial pressure of HCHO.	Relative reciprocal time.
100	1.00	50	1	50	1
200	2.98	100	3.09	100	1.48
300	4.94	150	9.84	150	2.02
				200	2.44
				300	3.15
				400	5.78
(b) Methane pressure constant at 200 mm.		(b) Methyl alcohol pressure constant at 100 mm.		(b) Formaldehyde pressure constant at 100 mm.	
Initial pressure of O ₂ .	Relative reciprocal time.	Initial pressure of O ₂ .	Relative reciprocal time.	Initial pressure of O ₂ .	Relative reciprocal time.
150	1.00	50	1	100	1.00
200	1.16	100	0.69	200	0.91
300	1.80	150	0.72	300	0.85
440	2.87	200	0.86	400	0.87
		250	0.93		
		300	0.85		
		400	1.11		

Every example given in the above table was duplicated, the average value being recorded. In all three cases the influence of the concentration of the combustible gas is very great, while except in the case of methane the influence of oxygen is small. The various relationships are illustrated in fig. 2.

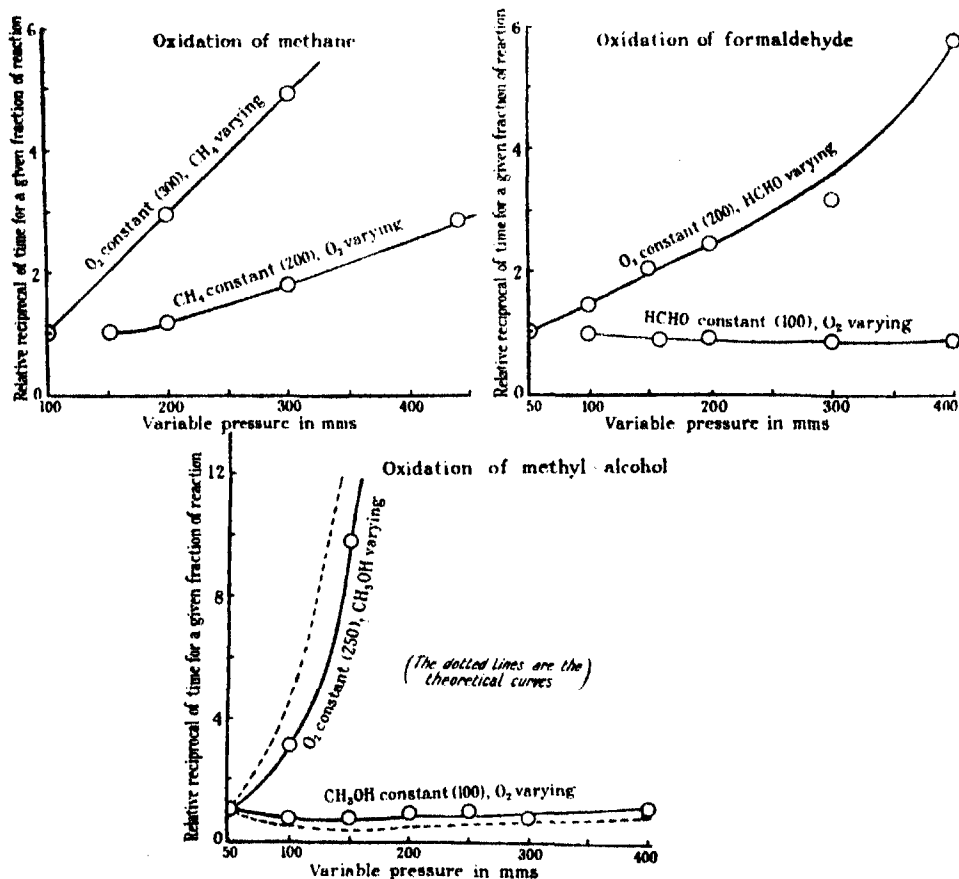


FIG. 2.

Influence of Surface.

If reaction chains start in the gas phase and end at the wall of the vessel, then the reaction will be much lower in a vessel of small than in one of large dimensions. But if the chains end mostly in the gas the size of the vessel will be unimportant. All three reactions here studied are slowed down considerably by a sufficient increase in the surface of the vessel.

With methane, for example, the following result is typical:—

150 mm. CH_4 : 298 mm. O_2 , 467°.
Silica bulb. Time for 50 per cent. of total pressure increase 5.5 minutes.

150 mm. CH_4 : 298 mm. O_2 , 467°.
Similar silica bulb packed with silica tubes, 15 per cent. increase in 60 minutes. Analysis of gas withdrawn CO_2 , 0.4 per cent.; CO , 4.9 per cent.; O_2 , 61.5 per cent.; CH_4 , 33.2 per cent.

In a vessel filled with small silica spheres the reaction would not proceed at all in 30 minutes under the above conditions, analysis of the gas withdrawn showing neither carbon monoxide nor dioxide.

Askey* has shown that the oxidation of formaldehyde, like that of benzaldehyde, occurs much more slowly in a bulb packed with silica powder than in an empty one. This was confirmed by the observation that in our bulb packed with silica spheres the reaction would hardly take place at 297°.

In the bulb packed with tubes the results with formaldehyde were very erratic. This fact, though disadvantageous from an experimental point of view, is very significant. It shows that the rate of reaction is governed not only by the extent of the surface and the dimensions of the vessel but by the qualitative nature of the wall. The variability of the latter factor is probably due to variations in the adsorbed gas layers. In this connection the following two facts are important. First, Pease† has shown that washing reaction vessels with a solution of potassium chloride markedly alters rates of oxidation. Secondly, it appeared in the course of this present series of experiments that the velocity of reaction in a new bulb often varied in the course of the first few experiments and then settled down to a constant value.

A more detailed investigation of the relation between the rate of reaction and the size of the vessel was made with methyl alcohol; the results are described in the following section.

Relation between Reaction Rate and Size of Vessel in the case of Methyl Alcohol.

Comparison with the case of Benzene.

Two series of experiments were made. In the first series vessel A was of silica and of about 180 c.c. capacity, approximately cylindrical, length 10 cm., diameter 5.9 cm. Vessel B was also cylindrical, length 9.5 cm., diameter 6.7 cm., but being entirely packed with lengths of silica tubing of internal diameter 1 cm., offered only about one-sixth of the distance for the chains to travel before meeting the wall.

Temperature 437° C.	100 mm. CH ₃ OH, 200 mm. O ₂ .			
Half life in vessel A (minutes)	3.5	3.5	3.5	3.9
Half life in vessel B (minutes)	17.8	14.2	16.6	17.6

These two bulbs had had very different previous histories. Therefore, a set

* 'J. Amer. Chem. Soc.,' vol. 52, p. 974 (1930).

† *Ibid.*, vol. 51, p. 1839 (1929).

of new bulbs of varying diameter but all of length 9 cm. and of the same silica were obtained. The following results were obtained with them.

100 mm. CH_3OH , 200 mm. O_2 .

Temperature.	Time required for reaction to go from 20 to 80 per cent. (minutes).			
	7.5 cm. diameter.	4.9 cm. diameter.	3.2 cm. diameter.	1.8 cm. diameter.
•				
427	6.6	25.5	59	Too long to measure. No experiment. (Anomalous 3.3.)
447	1.7	13.0	25.4	
463	0.80	4.8	14.6	

It can be shown that if reaction chains start in the gas and are broken whenever they reach the wall but never in the gas, then the rate of reaction should be approximately proportional to the square of the diameter of the vessel, if this is cylindrical and fairly long in comparison with its radius. The theory, however, leaves out of account possible qualitative differences between one vessel and another in regard to the efficiency with which the surface can break chains when they arrive there.

The above two series of results are not by any means in quantitative agreement with the simple theory, but in spite of this they show without any reasonable doubt that the chains must normally end on the walls, and thus may be of considerable length.

In a previous paper on the oxidation of benzene we concluded that the oxidation was only influenced by the dimensions of the vessel when these became very small (bulb packed with small spheres), and therefore that the chains were broken principally in the gas. The striking contrast between these results and the present results with methyl alcohol led us to repeat the benzene experiments with the four new bulbs.

Temperature 527°. 100 mm. benzene, 300 mm. oxygen.

Diameter of bulb (cm.)	7.5	4.9	3.2	1.8
Half life (minutes)	9.1	10.5	(20)	13.3

The existence of the very striking contrast in behaviour is thus confirmed.

The influence of nitrogen on the oxidation of methyl alcohol is to cause a

small but definite acceleration of 30 to 40 per cent. for a pressure of nitrogen equal to that of the oxygen. The effect of a foreign gas is two-fold; it hinders the chains from reaching the walls, and it may itself deactivate. Thus the resultant effect is unpredictable.

Influence of Temperature.

In deriving the heats of activation the logarithm of the time required for the reaction to go from 20 to 80 per cent. was plotted against $1/T$ in the case of methane, while the logarithm of the half-life was plotted in the other two cases, since the influence of the induction period on the results is negligible.

Methane. CH ₄ 150 mm. O ₂ 300 mm.			Methyl alcohol. CH ₃ OH 100 mm. O ₂ 200 mm.			Formaldehyde. HCHO 100 mm. O ₂ 200 mm.		
Tempera- ture ° C.	<i>t</i> obs. (mins.).	<i>t</i> calc.	Tempera- ture ° C.	<i>t</i> obs. (mins.).	<i>t</i> calc.	Tempera- ture ° C.	<i>t</i> obs. (mins.).	<i>t</i> calc.
487	0.95	0.95	452	2.65	2.63	337	2.6	2.55
467	2.65	2.74	444	4.15	4.31	327	3.4	3.43
457	4.54	4.98	437	6.5	6.6	307	6.2	6.1
447	12.7	9.1	429	10.0	11.2	297	8.4	8.3
			422	18.9	17.4	287	11.3	11.5
			407	42.4	47.0			
E = 61,500 calories.			E = 62,500 calories.			E = 20,600 calories.		

$t_{\text{calc.}}$ is obtained from the Arrhenius equation using the value of E given in the table. The low value of E for formaldehyde is to be noted in connection with the low temperature at which the reaction takes place. Though no definite correlation can be expected in chain reactions, the influence of the exponential factor in which E occurs must always be pronounced.

Approximate Quantitative Treatment of the Oxidation of Methyl Alcohol.

The evidence of an earlier section shows that the chains start in the gas and are broken at the walls.

The other two facts on which the theory is based are the very marked influence of methyl alcohol concentration on the rate, and the small influence of oxygen. The first leads us to assume that chains are continued when an active intermediate substance, X , collides in the gas phase with more methyl

alcohol molecules ; the second indicates that oxygen has a deactivating effect which counteracts its normal influence as a reacting substance.

Since the chains are broken at the wall, we assume the deactivating influence of the oxygen to be exercised there ; that is, that the active molecules X are destroyed by reaction with adsorbed oxygen. This allows for the possibility of qualitative variations in the effectiveness of different surfaces.

Attention will be confined to the state of affairs prevailing after the induction period is over.

We have

$$\frac{-d[\text{CH}_3\text{OH}]}{dt} = k_1[\text{CH}_3\text{OH}][\text{O}_2] + k_2[X][\text{CH}_3\text{OH}],$$

(1)
(2)

$$\frac{d[X]}{dt} = k_1[\text{CH}_3\text{OH}][\text{O}_2] - k_2[X][\text{CH}_3\text{OH}] + k_3[X][\text{CH}_3\text{OH}]$$

(3)
(4)
(5)

$$-k_3 \frac{[X][\text{O}_2]^n}{[\text{CH}_3\text{OH}]^m} = 0.$$

(6)

(1) represents the initiation of the chain by a collision between methyl alcohol and oxygen forming X , and (2) its continuation by collision between X and methyl alcohol. (3) corresponds to (1) and (4) to (2) while (5) is introduced to express the fact that each X which disappears by reaction with methyl alcohol ultimately regenerates another X to continue the chain. (6) represents the breaking of the chain by oxidation of X on the wall. The rate of this depends on the amount of adsorbed oxygen, which will be a function of the oxygen concentration and of that of any competing gases, in this case of methyl alcohol itself. The two terms with the fractional powers n and m are intended to allow for this in a rough empirical way, but, as is obvious, the necessity for considering the adsorption equilibrium makes an exact treatment impossible. We will make a trial with m and n equal to unity for the sake of simplicity.

k_3 will be inversely proportional to the total pressure, since X diffuses less easily to the wall when the pressure is high.

Solving the equations and remembering that process (2) accounts for very much more of the reaction than process (1) we find

$$\frac{-d[\text{CH}_3\text{OH}]}{dt} = k[\text{CH}_3\text{OH}]^2 [\text{Total pressure}].$$

If a and b are the initial amounts of methyl alcohol and oxygen, and x the amount of methyl alcohol oxidised at time t ,

$$\frac{dx}{dt} = k(a - x)^2(a + b + x),$$

the total pressure being $a + b + x$ since $\text{O}_2 + \text{CH}_3\text{OH} = \text{CO} + 2\text{H}_2\text{O}$.

$$kt = \frac{1}{(2a + b)} \cdot \frac{1}{2} \left\{ \frac{1}{(a - x)^2} - \frac{1}{a^2} \right\} + \frac{1}{(2a + b)^2} \left\{ \frac{1}{a - x} - \frac{1}{a} \right\} + \frac{1}{(2a + b)^3} \left\{ \log \frac{a}{a - x} + \log \frac{a + b + x}{a + b} \right\}.$$

The half life values are obtained by putting $x = a/2$ when oxygen is in excess and $x = b/2$ when methyl alcohol is in excess.

The results yielded by this equation are shown by the dotted curves in fig. 2. In broad outline the experimentally found relations are reproduced, but from the nature of the assumptions that have to be made about the adsorption relationships precise agreement cannot be expected.

No attempt was made to express mathematically the course of the curves in fig. 1. It may be remarked, however, that in a given experiment the rate does not fall off, as reaction proceeds, in as marked a manner as the influence of the initial pressure would lead one to anticipate. This may be due to the fact that the products of reaction displace oxygen from the surface and render it much more active. This effect would act in opposition to that of the falling methyl alcohol concentration. It is, of course, not allowed for in the above equation—which is therefore only applied to calculate the influence of the initial pressures.

Presumably consideration similar to the above apply to the other two oxidations, and it will be evident that from the number of factors which influence the rate of reaction the specific differences between one substance and another are easily understood, though unpredictable.

General Considerations.

Certain general conclusions emerge from these investigations which can be summarised as follows.

The much greater influence of hydrocarbon concentration than of oxygen concentration on the rate of reaction already found with ethylene and benzene appears to be general. In the theoretical treatment we have attributed this to a deactivating influence of oxygen.

All the reactions are chain reactions, but the length of chain and the method by which it is ended vary considerably from one reaction to another. With benzene, for example, the chains do not appear to reach the walls unless the free space in the vessel is very small, while with methyl alcohol nearly all the chains appear to end there.

The actual nature and condition of the wall have a considerable influence. With methyl alcohol, in order to account for the experimental results, we have been led to assume that the efficiency of the walls in breaking chains depends upon the layer of adsorbed oxygen.

The existence of a variety of methods by which chains are broken, and especially the probability that surface adsorption relations play a part accounts for the considerable divergences in the behaviour of different substances.

Incidentally, the very different extents to which the rate of oxidation of different substances is affected by the dimensions of the vessel may not be without practical significance in connection with the combustion of gaseous fuels.

Summary.

The peculiarities associated with gaseous oxidation reactions, such as that of ethylene or of benzene have been further investigated, with a view to discovering the part played by chemical configuration in determining the kinetics of the oxidation. The substances studied were methane, methyl alcohol and formaldehyde, the two latter being intermediate products in the oxidation of the former.

The following characteristics were common to all the reactions: an initial induction period, most pronounced with methane; the striking dependence of the rate of reaction on the concentration of the combustible gas, and the relatively small influence of oxygen concentration; the marked decrease in the rate of reaction in vessels of small dimensions.

These characteristics are best explained by assuming that the reactions occur by "chain" mechanism.

The operation of this mechanism does not seem to depend upon any particular chemical configuration of the reacting molecules, as long as the necessary energy is available.

The relation between rate and the dimensions of the vessel has been studied in detail for methyl alcohol, in the oxidation of which the chains appear to end only at the wall of the vessel, in contrast with the case of benzene where they end principally in the gas unless the vessel is very small.

The part played by the walls depends not only on the dimensions of the vessel but on the nature of the surface. It seems probable that the adsorbed layer of oxygen may play an important part in breaking the chains which reach the wall.

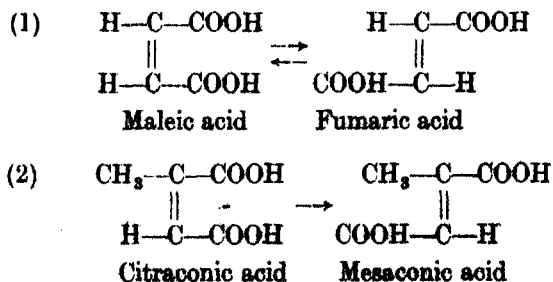
A theory based upon these assumptions gives results in general agreement with experiment.

Geometrical Inversion in Light.

By BHADRAMUKH K. VAIDYA, M.Sc. (Bombay).

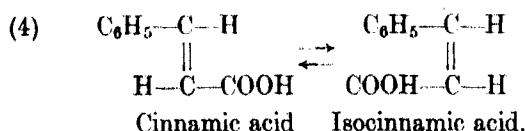
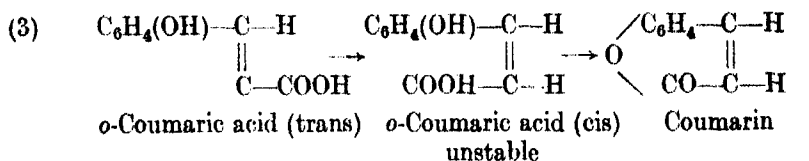
(Communicated by E. C. C. Baly, F.R.S.—Received July 8, 1930.)

One of the most interesting types of photochemical change is exhibited by the class of organic compounds known as geometrical isomers. Under the influence of ultra-violet radiation these substances change from the *cis*-form to the *trans*-form and *vice versa*. Although many compounds of this class are known, no quantitative investigation has been made of the relation between the light energy absorbed and the amount of change produced except in the case of maleic and fumaric acids. This pair of geometrical isomers was investigated by Warburg,* who found a very low quantum efficiency for the change in both directions. Volmar,† however, stated that maleic-fumaric acids and citraconic-mesaconic acids underwent a decomposition of the same nature as oxalic and malonic acids, where carbon dioxide is one of the products of decomposition. The present investigation was undertaken to study the photochemical change in as many compounds of this type as possible, and the following pairs of isomers were examined :—



* 'Sitzungsber. Preuss. Akad. Wiss.,' vol. 50, p. 960 (1919).

† 'C. R.,' vol. 181, p. 467 (1925).



Preparation of the Materials.—Maleic and fumaric acids were obtained from the British Drug Houses. The former was purified by repeated recrystallisations from conductivity water and the latter re-sublimed three times and collected as a white powder. The melting point of the maleic acid was 134°.

Merck's citraconic acid was purified by several crystallisations from chloroform and washed with ether. Melting point 92°.

Mesaconic acid was prepared from citraconic acid by exposing a saturated solution in chloroform, containing a trace of bromine, in a large quartz test tube to the radiations from a mercury vapour lamp. In a few minutes about 60 per cent. of the acid was precipitated as mesaconic acid. This after washing with chloroform and ether was recrystallised from alcohol. Melting point 214°.

o-Coumaric acid, coumarin and cinnamic acid were British Drug Houses products. They were recrystallised several times from hot conductivity water. Melting point 208°, 70° and 133° respectively.

Iso-cinnamic acid was prepared from cinnamic acid by exposing a saturated solution of the latter in methyl alcohol to ultra-violet light for 5 days, when about 25 to 30 per cent. of the acid was converted into the iso- or the cis-form. After evaporating the solution the residue was extracted several times with cold petroleum ether. The solvent was then allowed to evaporate slowly, when colourless crystals of iso-cinnamic acid melting at 42° were obtained.

All the solutions were made up in freshly prepared conductivity water.

As Volmar's results appeared rather unusual in the light of the work by previous investigators, an attempt was made to repeat his experiments. According to him, maleic, fumaric and citraconic acids, besides undergoing a partial inversion under the influence of light, also decompose into carbon dioxide and monobasic acids of the acrylic acid series. Aqueous solutions of these acids of the same strength (0.015 molar) as employed by Volmar were irradiated by ultra-violet light for 6 hours in a quartz cell connected with a

small eudiometer. It was found, however, that no trace of gas whatever was evolved and that the exposed solutions did not develop any odour peculiar to acrylic and crotonic acids.

Apparatus and General Procedure.—The source of radiation was a U-shaped quartz mercury vapour lamp operated at 2 amps. and 200 volts. The lamp was enclosed in an air-cooled box having a circular aperture 2 inches in diameter in front. Outside the box and at a distance of 4 inches from the aperture was fixed a large quartz condenser (focal length 4 inches) fitted with an iris diaphragm. The emergent beam of light was slightly divergent. The condenser and the diaphragm followed by a 4 cm. rectangular quartz cell containing water, holders for various light filters, the photochemical cell and the thermopile, were all fixed on an optical bench carrying a scale.

The quartz photochemical cell made by the Thermal Syndicate Company was cylindrical in shape, 3.80 cm. long and 2.60 cm. wide, the exposed area being 5.31 sq. cm. It was also provided with an outer jacket through which water was syphoned from the thermostat. The whole cell was made in one piece.

A Wratten ultra-violet filter was used for the mercury lines at 365 $\mu\mu$ and Chance Bros. ultra-violet glass (1 mm. thick) was used in conjunction with 1 cm. thickness of 0.001 N potassium chromate solution* in a quartz cell for the lines at 313 $\mu\mu$. These gave practically monochromatic radiations. Spectrophotometric determinations showed that the Wratten filter transmitted only 43.2 per cent. of 365 $\mu\mu$ radiations, whilst the transmission of the 313 $\mu\mu$ group of lines through the ultra-violet glass and potassium chromate solution was 79.4 per cent. In the preliminary experiments, however, it was found that the Wratten filter was of little use, since the substances examined have an extremely low absorption for the wave-length 365 $\mu\mu$. This, added to the low transmission of the filter, rendered the energy measurements difficult, and consequently the determination of the quantum efficiency for this wave-length was abandoned.

Measurements of the absorption of energy were carried out with a Hilger linear thermopile (20 Bi-Ag junctions) and a Moll galvanometer having an electric control magnet. The thermopile was calibrated with a Hefner lamp standardised by the National Physical Laboratory. The candle-power of this lamp under 760 mm. pressure and with air containing 8.8 litres of moisture per cubic metre was equivalent to 0.915 international candle with a possible error of 1 per cent. As the energy given out by the standard Hefner is

* Weigert, "Optische Methoden der Chemie," Leipzig, 1928.

900 ergs per square centimetre per second at a distance of 1 metre, and is equivalent to 0.90 international candle, the energy given out by the lamp used was 915 ergs per square centimetre per second at 1 metre distance. The calibration of the thermopile was carried out every fortnight during the investigation in a room entirely free from draughts, under the conditions specified by Gerlach* and Coblentz.† The type of the galvanometer used gave a very stable zero and was not at all affected by outside vibrations. As a mean of 25 determinations the value obtained for the galvanometer deflection was 67 mm. for a distance of 1 metre between the Hefner lamp and the thermopile. This corresponds to 13.65 ergs for a deflection of 1 mm.

The end of the photochemical cell exactly covered the brass tube holding the thermopile so that only those radiations transmitted by the liquid in the cell were received by the instrument. Since the change produced in maleic, fumaric and citraconic acid solutions was never greater than 4 per cent. even after long exposures, and since cinnamic, isocinnamic and coumaric acids at the concentrations and thickness used totally absorbed 313 $\mu\mu$ radiations, practically no difference was observed in consecutive galvanometer deflections except for the slight fluctuations due to the variation in the intensity of the mercury arc, which, however, did not amount to more than 2 mm. Galvanometer deflections were noted every half hour during each experiment. For the calculation of the total energy absorbed the mean value of the galvanometer readings was taken. At the end of each experiment the solution in the cell was replaced by distilled water and its transmission noted. The difference between the transmission by water and by the solution would then correspond to the amount of energy absorbed by the solution in terms of galvanometer readings. A small correction due to the loss of energy by reflection at the quartz/liquid and air/quartz surfaces was applied in the final calculations of the total energy absorbed.

Absorption Spectra.—The absorption spectrum of each of the solutions was determined by the spectrophotometer. Maleic, fumaric, citraconic and mesaconic acids show only general absorption in the ultra-violet with small molecular coefficients, whilst the curves for *o*-coumaric, cinnamic and isocinnamic acids show a very high selective absorption. Coumaric acid has two bands, one at 315 $\mu\mu$ and the other at 268 $\mu\mu$, the intensity of the former being about half that of the latter. Cinnamic and isocinnamic acids have each only one band of high intensity at 270 $\mu\mu$ and 252 $\mu\mu$ respectively.

* 'Phya. Z.', vol. 14, p. 577 (1913).

† 'Bull. Bureau Stand.', vol. 11, p. 87 (1914).

In Table I the percentage transmissions of $313\text{ }\mu\mu$ radiations through a 4 cm. layer for all the solutions investigated as determined by the thermopile and photographic methods are compared. For the calculation by the thermopile method transmission through pure water is taken as 100 per cent., as the absorption of $313\text{ }\mu\mu$ radiations by water is very small. In the Table, T_1 and T_2 are the percentage transmissions as measured by the thermopile and spectrophotometric methods respectively. The solutions of *o*-coumaric, cinnamic and isocinnamic acids at the concentration and thickness employed showed no transmission by either of the methods.

Table I.

Acid.	Maleic.		Fumaric.		Citraconic.		Mesaconic.	
Conc. mol. lit.	0.01	0.005	0.01	0.005	0.01	0.005	0.01	0.005
T_1	35.0	60.0	37.5	61.7	82.5	90.9	64.6	79.2
T_2	39.8	63.1	42.7	65.3	87.1	93.3	69.2	83.2

Conductivity Measurements.—The change in all cases was followed by conductivity measurements on a Wheatstone bridge. The bridge wire was carefully calibrated and all the readings were taken near the middle of the bridge. The source of the alternating current was a Nernst coil, and after a little practice a sharp minimum could easily be obtained with the telephone. An Arrhenius type of conductivity cell made of boro-silicate glass with platinum electrodes 2.5 cm. in diameter was employed. The distance between the electrodes was fixed to suit the particular electrolyte. The accuracy of the standard coil resistances employed was 1 in 2000. The cell was placed in an electrically controlled thermostat which maintained a temperature constant to within 0.01°C . The cell constant was determined from time to time with a standard solution of potassium chloride. As it was only necessary to obtain relative measurements the use of a more elaborate apparatus was not necessary. For comparison with Ostwald's data, measurements at 18° and 28° were carried out, and from these the molecular conductivity was calculated at 25°C . The results are shown in Tables II and III.

Table II.—Cell constant 0.3701. R_t and μ_t are resistances and molecular conductivity, respectively. C is the temperature coefficient in the formula: $\mu_{25} = \mu_{18} (1 + C_{18-25})$.

Acid.	Maleic.		Fumaric.		Citraconic.		Mesaconic.	
Conc. mol. lit.	0.01	0.005	0.01	0.005	0.01	0.005	0.01	0.005
R_{18}	168.2	289.1	409	616	237.3	387.5	441.1	679
R_{25}	117.0	247.5	355.2	529	210.0	231.3	393.0	570
μ_{18}	220.1	256.0	90.5	120.2	156.0	191.0	83.9	109.0
μ_{25}	257.2	300.0	104.2	140.0	176.2	223.4	94.2	129.8
$C_{18-25} \times 10$	0.1686	0.1720	0.1514	0.1524	0.1295	0.1691	0.1227	0.1906
μ_{25} (calc.)	246.1	286.6	100.1	133.0	170.2	213.6	91.1	123.5
μ_{25} (obs.)	247	287	101	136	171	214	93.5	126

Table III.—Cell constant 0.1762.

Acid.	Cinnamic.		Isocinnamic.		o-Coumaric.	
Conc. mol. lit.	0.003	0.002	0.003	0.002	0.005	0.002
R_{18}	—	2120	855	1100	—	2888
R_{25}	1397	1857	787	1009	1432	2378
μ_{18}	35.5	41.5	68.7	80.1	—	30.5
μ_{25}	41.0	47.4	74.6	87.3	24.6	37.0
$C_{18-25} \times 10$	0.1422	0.1422	0.0859	0.0899	—	0.2131
μ_{25} (calc.)	—	45.6	72.8	85.1	—	35.0
μ_{25} (obs.)	39.7	47	74	87	—	36.8

The percentage change or conversion of one isomer into the other on exposure to light was determined by measuring the conductivity of the mixture of a pair of isomers containing varying amounts of each corresponding to the range of change produced. These measurements are shown in Tables IV, V, VI, VII and VIII. The calculated value of the specific conductivity in the last column of each table was obtained from the well-known isohydric formula of Arrhenius. All the values given are for 18° C., except those of 0.003 M cinnamic acid and isocinnamic acids and 0.005 M o-coumaric acid, which are for 28° C.

Table IV.—Maleic : fumaric acid mixture. R = resistance. k = specific conductivity $\times 10^3$.

Conc. Molar.		0.01			0.005		
Vol. c.c. Mal. : Fum.	p.c. Maleic.	R.	k (Obs.).	k (Calc.).	R.	k (Obs.).	k (Calc.).
20 : 0.0	100	168.2	2.2003	—	289.1	1.2800	—
20 : 0.2	99.01	169.2	2.1874	2.1882	290.8	1.2727	1.2735
20 : 0.4	98.03	170.2	2.1745	2.1743	292.2	1.2666	1.2668
20 : 0.6	97.09	171.1	2.1630	2.1623	293.9	1.2595	1.2602
0 : 0.20	0.00	409.0	0.9049	—	616.0	0.6003	—

Table V.—Fumaric : maleic acid mixture.

Conc. Molar.		0.01			0.005		
Vol. c.c. Fum. : Mal.	p.c. Fumaric.	R.	k (Obs.).	k (Calc.).	R.	k (Obs.).	k (Calc.).
20 : 0.0	100	409.0	0.9049	—	616.0	0.6003	—
20 : 0.2	99.01	403.2	0.9180	0.9177	609.2	0.6075	0.6070
20 : 0.4	98.03	397.8	0.9304	0.9335	604.0	0.6127	0.6137
20 : 0.6	97.09	392.6	0.9424	0.9427	597.0	0.6198	0.6201
20 : 0.8	96.15	387.6	0.9548	0.9549	590.5	0.6266	0.6265
0 : 0.20	0.00	168.2	2.2003	—	289.1	1.280	—

Table VI.—Citraconic : mesaconic acid mixture.

Conc. Molar.		0.01			0.005		
Vol. c.c. Cit. : Mes.	p.c. Cit.	R.	k (Obs.).	k (Calc.).	R.	k (Obs.).	k (Calc.).
20 : 0.0	100	237.3	1.5596	—	387.0	0.9550	—
20 : 0.2	99.01	238.4	1.5524	1.5523	388.3	0.9532	0.9524
20 : 0.4	98.03	239.5	1.5450	1.5455	390.5	0.9478	0.9482
20 : 0.6	97.09	240.5	1.5388	1.5394	392.0	0.9440	0.9444
0 : 0.20	0.00	441.0	0.8392	—	679.0	0.5450	—

Table VII.—Cinnamic : isocinnamic acid mixture.

Conc. Molar.		0.003			0.002		
Vol. c.c. Cin. : Iso.	Cin.	R.	k (Obs.).	k (Calc.).	R.	k (Obs.).	k (Calc.).
20 : 0.0	100	1397	0.1264	—	2120	0.0831	—
20 : 2.0	90.91	1308	0.1347	0.1354	1949	0.0904	0.0901
20 : 5.0	80.00	1202	0.1467	0.1458	1783	0.0989	0.0958
20 : 8.0	71.41	1146	0.1537	0.1542	1674	0.1052	0.1051
20 : 13.0	60.61	1065	0.1655	0.1647	1558	0.1131	0.1135
10 : 10.0	50.00	1001	0.1760	0.1751	1443	0.1221	0.1217
10 : 15.0	40.00	958	0.1839	0.1848	1364	0.1292	0.1294
10 : 23.0	30.30	903	0.1951	0.1943	1283	0.1373	0.1368
5 : 20.0	20.00	859	0.2051	0.2043	1215	0.1450	0.1448
0 : 20.0	0.00	787	0.2238	—	1100	0.1602	—

Table VIII.—*o*-Coumaric acid : coumarin mixture.*

Conc. Molar.		0.005.		0.002.	
Vol. c.c. Acid : Coum.	p.c. Acid.	R.	k .	R.	k .
20 : 0	100	1432	0.1230	2888	0.0610
20 : 0.5	97.55	1452	0.1213	2930	0.0601
20 : 1.0	95.25	1473	0.1196	2969	0.0593

* Coumarin, being non-conductive, has merely the effect of dilution.

Standard curves for the variation in conductivity with the composition of the mixture were obtained for each of the systems and the amount of change produced after the exposure was then directly read off from the particular curve.

Besides the conductivity method it was also possible in the case of the cinnamic acid to follow the change spectroscopically. Here, as the change produced is considerable, a measurable displacement of the absorption curve takes place. In fig. 1, A and B are the absorption curves of cinnamic and isocinnamic acids respectively. A theoretical curve C is constructed from A and B corresponding to a mixture of 50 per cent. of each of the two acids. Curve D obtained for a solution of cinnamic acid which had been exposed for $4\frac{1}{2}$ hours to $313 \mu\mu$ radiations and which showed a 50 per cent. change by the conductivity measurements. It will be seen that the curves C and D almost coincide.

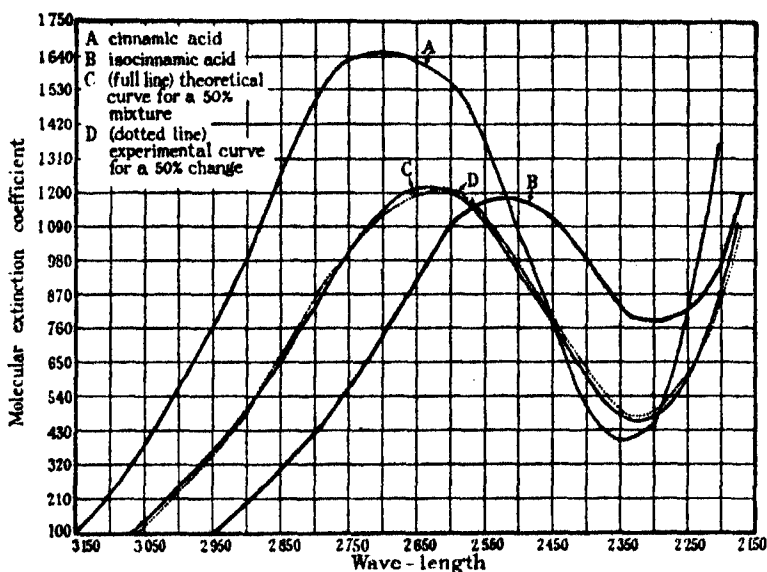


FIG. 1.

Velocity of the Change.—Velocity measurements were carried out for the cinnamic-isocinnamic acid and the reverse changes as these were the only cases out of the five studied where good differences in resistance were obtained with varying times of exposure. Results for 0.003 and 0.002 M cinnamic and isocinnamic acid solutions are shown in Table IX.

Table IX.

Acid	Cinnamic.				Isocinnamic.			
	0.003 M.		0.002 M.		0.003 M.		0.002 M.	
Time (hrs.).	R.	p.c. change.	R.	p.c. change.	R.	p.c. change.	R.	p.c. change.
0	1397	0	2120	0	787	0	1100	0
1	1308	8.8	1892	12.9	794	3.1	1120	3.5
2	1230	17.1	1702	26.6	800	5.7	1137	6.2
3	1158	25.9	1569	38.1	814	9.6	1148	9.8
4	1100	34.0	1478	46.5	820	11.3	1168	13.2
5	1045	43.2	1405	55.3	834	14.8	1196	16.4
7	965	57.6	1272	71.5	852	21.0	1223	23.7
10	867	71.8	1246	75.2	893	27.9	1254	25.8

In fig. 2 the percentage change for all the four solutions is plotted against the time of exposure. It will be seen that the rate of change is directly pro-

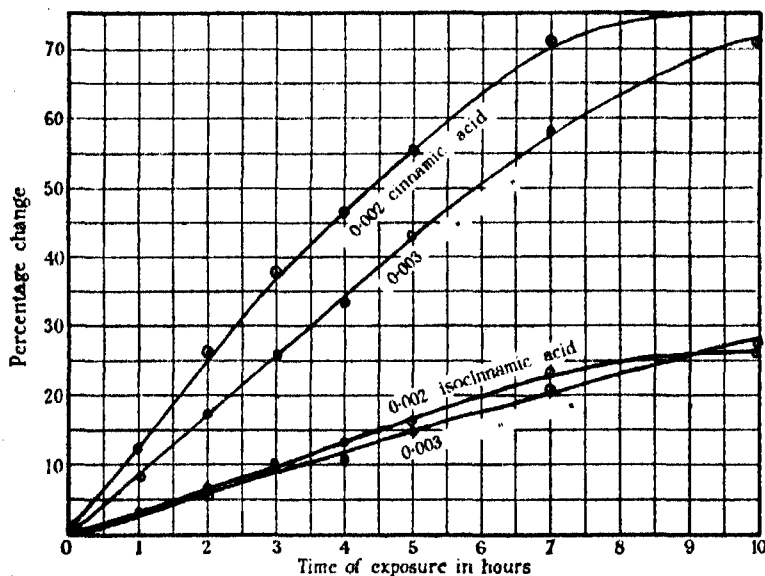


FIG. 2.

portional to the time of exposure for the first 5 hours, after which it gradually falls off till the equilibrium point is reached, when the system becomes stationary. The direct as well as the reverse reaction thus belongs to the zero order.

The equilibrium point which may be attained from either direction after about 10 hours' exposure, corresponds to 72 per cent. of isocinnamic acid in the case of a 0.003 M solution and 75 per cent. in the case of a 0.002 M solution.

The Quantum Efficiency of the Change.—Each of the quantum efficiency determinations was repeated at least once, the calculations being made as follows :—

$$E = g.H.t.A.f.\lambda/h.c. \quad M = N.m.P.V./100.1000 \quad M/E = \phi,$$

where E = total number of quanta absorbed, g = galvanometer deflection (difference between water and solution), H = Hefner value, that is the energy corresponding to 1 mm. deflection = 13.65 ergs per square centimetre per second, t = time of exposure in seconds, A = exposed area of the cross section of the cell, 5.31 sq. cm., f = factor for correction of loss of energy due to reflection at two quartz/liquid and one quartz/air junction = 1.06, λ = wave-

length of the radiation = 3130×10^{-8} cm., h = Planck's constant = 6.55×10^{-27} , c = velocity of light = 3×10^{10} cm. per second, M = total number of molecules changed, N = Avogadro's number = 6.06×10^{23} , m = concentration of the original solution exposed in gram. molecules per litre, P = percentage change, V = volume of the liquid in the cell = 20.66 c.c., ϕ = the quantum efficiency.

Substituting various values,

$$E = g \cdot t (0.1224 \times 10^{14}) \quad M = P \cdot m (125.2 \times 10^{18}).$$

The complete data and quantum efficiency results are shown in Table X.

Table X.

Acid.	m Conc.	t hrs.	R before.	R after.	P.	$M \times$ 10^{18}	g mm.	$E \times$ 10^{18}	ϕ	ϕ mean.
Maleic	0.01	10	168.2	169.6	1.4	1.75	78	34.37	0.051	0.048
	0.01	10	168.2	169.4	1.2	1.50	76	33.48	0.045	
Maleic	0.005	10	289.1	291.8	1.8	1.13	48	21.15	0.053	0.0525
	0.005	10	289.1	291.8	1.8	1.13	49	21.59	0.052	
Fumaric	0.01	10	409.0	391.6	3.1	3.88	75	33.04	0.117	0.1175
	0.01	10	409.0	391.0	3.2	4.01	77	33.94	0.118	
	0.005	10	616.0	597.6	2.8	1.75	46	20.27	0.086	0.083
	0.005	10	616.0	599.0	2.6	1.63	46	20.27	0.080	
Citraconic	0.01	12	237.3	239.0	1.6	2.00	21	11.10	0.180	0.182
	0.01	12	237.3	238.8	1.4	1.75	18	9.51	0.184	
	0.005	12	387.5	390.3	2.1	1.31	11	5.82	0.225	0.219
	0.005	12	387.5	389.9	1.8	1.13	10	5.29	0.213	
Coumaric	0.005	5	1432	1442	1.2	0.75	120	26.44	0.028	0.0305
	0.005	5	1432	1443	1.4	0.88	120	26.44	0.033	
	0.002	5	2888	2928	2.3	0.58	120	26.44	0.022	0.0225
	0.002	5	2888	2926	2.4	0.60	120	26.44	0.023	
Cinnamic	0.003	5	1397	1045	43.2	16.22	120	26.44	0.615	0.6095
	0.003	5	1397	1050	42.5	15.96	120	26.44	0.604	
	0.002	5	2120	1400	35.3	13.85	120	26.44	0.525	0.5305
	0.002	5	2120	1391	56.6	14.17	120	26.44	0.536	
Iso-cinnamic	0.003	5	787	834	14.8	5.55	120	26.44	0.210	0.206
	0.003	5	787	830	14.2	5.33	120	26.44	0.202	
	0.002	5	1100	1196	16.4	4.11	120	26.44	0.155	0.153
	0.002	5	1100	1189	15.9	3.98	120	26.44	0.151	

Discussion.—Before considering the general significance of the quantum efficiency results, we may briefly touch on some points in connection with the velocity of the change and the equilibrium.

It was shown by Warburg (*loc. cit.*) that it is possible to calculate the equilibrium position between two photoactive isomers from a knowledge of their quantum efficiencies and absorption coefficients. He calculated the equilibrium composition of the mixtures of maleic and fumaric acids from his own determinations of quantum efficiencies and it agreed with the values obtained experimentally by previous workers. Nearly the same value is obtained again from the results described in the present paper.

Still more interesting, however, is the case of equilibrium between cinnamic and isocinnamic acids where, unlike maleic-fumaric acids, the equilibrium is reached after about 10 hours' exposure, and, as shown in Table IX, it is possible to follow the reaction throughout its course. As the difference between the absorption coefficients of cinnamic and isocinnamic acids for the wave-length $313 \mu\mu$ is very small, the following relation holds :

$$dm_2/dt = I_0 A (\phi_1 - m_2/m_0 (\phi_1 + \phi_2)),$$

where m_2 is the concentration of the changing system at the time t , I_0 the intensity of the incident light, A the absorption of the system, ϕ_1 the quantum efficiency of the reverse change and ϕ_2 that of the direct change. At the stationary stage dm_2/dt is equal to zero and therefore,

$$m_2/m_0 = \phi_1/(\phi_1 + \phi_2).$$

Taking m_0 the original concentration of cinnamic acid as unity, m_2 the concentration of isocinnamic acid at the equilibrium, ϕ_1 the quantum efficiency of cinnamic acid and ϕ_2 that of isocinnamic acid, and substituting values from Table X, we obtain for 0.003 M solution $m_2 = 0.747$ or 74.7 per cent. and for 0.002 M solution $m_2 = 0.776$ or 77.6 per cent. After 10 hours' exposure the values obtained directly by experiment are 72 and 75 per cent. respectively, as seen before.

Wegscheider* has obtained a relation between the absorbed energy and the amount of change produced with time in an illuminated system. According to this with a photolyte absorbing a large amount of energy, the change is directly proportional to the time of exposure, or the reaction belongs to the zero order. On the other hand substances showing little absorption follow a reaction of the first order.

Cinnamic and isocinnamic acids which, as we have seen, totally absorb the incident light and follow the course of a reaction belonging to the zero order seem, therefore, to be ideal cases of one extreme which follow the Wegscheider relation.

Turning now to the results shown in Table X, it will be noticed that mesaconic

* 'Z. Phys. Chem.,' vol. 103, p. 273 (1913).

acid has been omitted. This, as well as crotonic acid, is known to be completely inactive towards light. Both these acids contain a methyl group in their molecules and probably it has a stabilising effect in a trans-molecule. Methylcoumaric acid, however, is known to change into the cis-form as easily as any other member of this class.* It would seem, therefore, that the methyl group in a trans-molecule when directly attached to a doubly linked carbon atom would strengthen the double bond and thus prevent the disruption of the molecule. In fumaric acid, which contains a hydrogen atom united to a doubly linked carbon atom in place of the methyl group in mesaconic acid, the rupture of the molecule by light is easier and therefore the strength of the double bond must be correspondingly weaker. This seems quite likely, as some recent calculations of Latimer† show. According to Latimer the repulsion energy between the kernels of two carbon atoms linked by a single bond ($\text{CH}_3 \cdot \text{C}$ as in mesaconic acid) is 1700 k. cals. whereas the repulsion energy between the kernels of a carbon and hydrogen atom ($\text{H} \cdot \text{C}$ as in fumaric acid) is only 500 k. cals. In a C—H bond, therefore, the linkage between the carbon and hydrogen being stronger, the rest of the carbon bonds would be weaker, whilst the C—C bond being relatively weaker, the remaining carbon bonds would be correspondingly stronger. This may account for the stability of mesaconic acid. Many organic reactions may be cited in support of this view. For example, it is known that the rate of addition of bromine is considerably less for mesaconic acid than for fumaric acid,‡ which means that the double bond is more difficult to break in the former than in the latter.

The effect of change of concentration on quantum efficiency is very marked in all cases. With the exception of maleic and citraconic acids, all the acids show in general a decrease in quantum efficiency with increase in dilution. This is like most of the other photochemical reactions where the amount of change produced depends on the frequency of collisions between the activated and the inactive molecules. Substances which show an increase in quantum efficiency with increase in dilution are rare but not unknown. Bodenstein§ found in the oxygen-ozone reaction a decrease in quantum yield with increase in pressure. In such cases it must be presumed that the activated molecule is either not sufficiently activated or its energy partly degrades in some other form on collision. Maleic and citraconic acids apparently belong to this class.

* Stoemer, 'Ber. D. Chem. Ges.,' vol. 42, p. 4865 (1909).

† 'J. Amer. Chem. Soc.,' vol. 51, p. 3185 (1929).

‡ Piutti, 'Rend. Accad. Sci. Fis. Nat., Napoli,' vol. 15, p. 18 (1922).

§ 'Z. Phys. Chem.,' vol. 85, p. 229 (1913).

The wide difference in quantum efficiency between cinnamic acid and the rest of the acids investigated is very marked. Warburg accounted for the low quantum efficiencies of maleic and fumaric acids by supposing that although one quantum brought about the disruption of the molecule in two parts, these parts instead of producing the isomer, reunited to form the original molecule in greater proportion than its isomer. If this explanation is accepted, the behaviour of *o*-coumaric acid, which also shows a very small quantum efficiency, must be accounted for in a similar way. From the results obtained with cinnamic acid, which differs very little from *o*-coumaric acid, it would seem that the mechanism of the change in these isomers is quite different from that attributed to them by Warburg.

The substances investigated may be divided into two classes, those in which the absorption is general and those in which it is selective. We have seen before that maleic, fumaric and citraconic acids show a general absorption and therefore belong to the first class, whilst coumaric, cinnamic and isocinnamic acids with selective absorption belong to the second class. As far as the present work is concerned, therefore, the substances showing general absorption have a low quantum efficiency, whilst those which show selective absorption have a higher value, unless the exciting radiations happen to be outside the absorption band. The behaviour of *o*-coumaric acid is exceptional for the following reasons.

In substances showing more than one absorption band a distinction between those which are photochemically active and those which are inactive is necessary. It seems to be generally true that the inactive bands are on the long wave side of the spectrum. On the other hand in an active band the quantum efficiency would tend to increase after the photochemical threshold is crossed and to go on rising on the short wave side till a maximum of one is attained. Some evidence for this view is furnished by Warburg's results* on potassium nitrate solutions, where the quantum efficiency for 313 $\mu\mu$ and 207 $\mu\mu$ are 0.02 and 0.25 respectively. Nitrates generally show two absorption bands, one at 313 $\mu\mu$ and the other in the far ultra-violet at about 200 $\mu\mu$. It would appear, therefore, that the first band is inactive, whilst the second one on the short wave side is active. Very similar results have been very recently recorded for benzoquinone solutions in water and alcohol.†

From an analogy of the behaviour of nitrates it would seem, therefore, that the first band at 315 $\mu\mu$ in *o*-coumaric acid is inactive, whilst the second one

* 'Z. Electrochem.,' vol. 54, p. 28 (1920).

† Leighton and Forbes, 'J. Amer. Chem. Soc.,' vol. 51, p. 3549 (1929).

on the short wave side at $268\text{ }\mu\mu$ would probably prove to be active, although this point could not be tested at present on account of the unsuitability of the mercury arc for the wave-length $268\text{ }\mu\mu$. When the absorption of *o*-coumaric acid is compared with that of cinnamic acid, it is seen that the original band suffers but a slight shift on the ultra-violet side, whilst a new band on the long wave side appears at $315\text{ }\mu\mu$, due to the substitution of the OH group in the molecule. Judging then from the high activity of cinnamic acid within its absorption band, it seems likely that the same band, slightly shifted in *o*-coumaric acid, would probably raise the quantum efficiency.

The activity of the single band in cinnamic acid is seen very clearly by a rise in quantum efficiency to about 20 times that with *o*-coumaric acid. Yet it falls short of unity, probably because at $313\text{ }\mu\mu$ where the absorption band starts the photochemical threshold has not been reached. For isocinnamic acid showing a comparatively lower quantum efficiency, $313\text{ }\mu\mu$ radiations lie just outside the absorption band, so that the quantum yield is not raised.

Summary.

1. Quantum efficiency determinations for the inversion of the following geometrical isomers have been made. Maleic and fumaric acids, citraconic acid, *o*-coumaric acid, cinnamic and isocinnamic acids. The mean respective values are 0.048, 0.117, 0.182, 0.030, 0.609, and 0.206, for the wave-length $313\text{ }\mu\mu$, with slight variations depending on the concentration of the solution.

2. It is suggested that in substances showing selective absorption, the quantum efficiency value would approach unity as the exciting radiation decreases in wave-length within one of the *photochemically active* bands. As far as the present work is concerned the substances showing general absorption or those in which the exciting radiation fails to fall within an active band, appear to have a low quantum efficiency.

3. Possible reasons for the inactivity of mesaconic acid and crotonic acid are discussed.

My thanks are due to Prof. E. C. C. Baly for his continued interest, encouragement and advice, and to Dr. R. A. Morton for his help in spectroscopic studies. I am also indebted to Dr. R. O. Griffith and Dr. A. McKeown for their interest and valuable criticism.

Lastly, I wish to express my gratitude to Sir Prabhashankar D. Pattani, K.C.I.E., Administrator, Bhavnagar State, India, for the grant of a travelling scholarship, which enabled me to undertake this work at the Liverpool University.

Gaseous Combustion in Electric Discharges. Part V.—A Spectrographic Examination of the Cathodic Combustion of Carbonic Oxide.*

By G. I. FINCH and H. H. THOMPSON, Imperial College of Science and Technology.

(Communicated by W. A. Bone, F.R.S.—Received July 14, 1930.)

[PLATE 18.]

Introduction.

The view previously put forward in Parts III and IV of this series, whilst affording a reasonable explanation of the known facts relating to the cathodic combustion of carbonic oxide "detonating gas,"† involved a sequence of collisions which must on kinetic grounds be rare, as Prof. S. Chapman, F.R.S., has since pointed out to us. This objection would no longer hold if charged atomic oxygen only be supposed to take part in the reaction. The question then arose as to whether oxygen atoms are, in fact, present within the cathode zone, and, also, whether such oxygen atoms and carbonic oxide do actually become ionised under the conditions of our previous experiments. The following spectrographic examination was therefore carried out in order to throw light on these matters.

The examination shows, amongst other results, that singly ionised oxygen molecules and atoms and neutral oxygen atoms are present within the discharge, but that carbonic oxide molecules, though strongly excited, are not ionised. These facts indicate the need of a complete revision of the view of the mechanism of the combustion of CO put forward previously in Parts III and IV of this series.

Experimental.

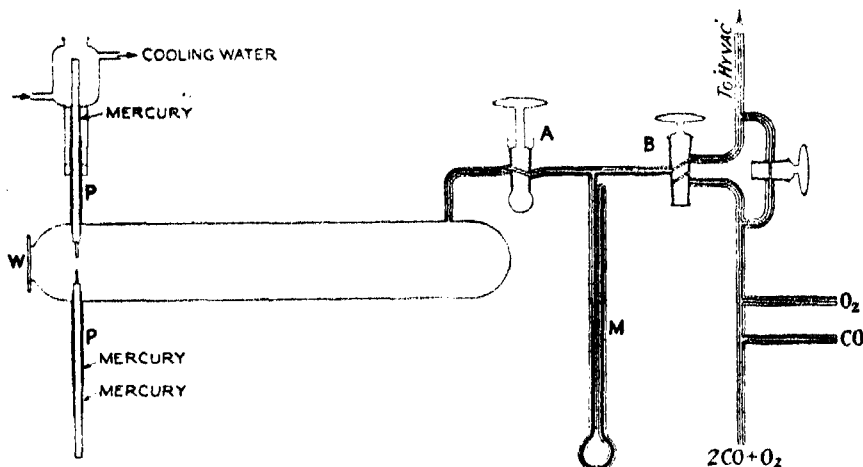
In the experiments about to be described steady direct current discharges, maintained between electrodes of various metals, were passed through "detonating gas," carbonic oxide, oxygen and steam, the discharges being examined by means of a Bellingham and Stanley quartz spectrograph.

* 'Proc. Roy. Soc.,' A, vol. 111, p. 257 (1926), (Part I); vol. 116, p. 529 (1927), (Part II); vol. 124, p. 303 (1929), (Part III); vol. 125, p. 352 (1929), (Part IV).

† A mixture of carbonic oxide and oxygen in their combining proportions will be referred to in what follows, for brevity, as "detonating gas."

Description of the Apparatus.

The electrical circuit employed was as previously described in Part III. The combustion vessel (see figure) consisted of a horizontally disposed cylindrical



glass vessel of 1100 c.c. capacity fitted with electrode ports, P, into which the electrode carriers were sealed with sealing wax, a quartz window, W, and the stopcocks, A and B, by means of which the vessel could be filled with the desired gas or gaseous mixture and placed in communication with the manometer, M. The upper electrode which served as cathode was water-cooled. In both cases, the sealing-waxed electrode port joints were sealed with mercury. The vessel contained 100 gms. of potassium hydroxide sticks, which served to dry the gas and also, in the case of "detonating gas," to remove the products of combustion.

The combustion vessel, an iron arc which could be swung into the position occupied by the discharge in the former, a 3-inch diameter quartz collecting lens, an iris diaphragm and the quartz spectrograph were clamped in riders mounted and lined up on a $1\frac{1}{2}$ m. optical bench.

The gases and mixtures employed were prepared in the manner previously outlined (Part III). In the case of the discharge in steam, however, the potassium hydroxide sticks contained in the discharge vessel were replaced by distilled water, and the vessel evacuated for sufficient time to enable the water vapour to sweep the vessel clear of impurities.

Experimental Procedure.

The optical system was set up in such a manner that the discharge image was accurately focussed on, projected upon, and in line with the spectrograph slit, the collecting lens being nearly midway between the discharge and the slit. Satisfactory definition in the image was secured by suitably closing down the iris diaphragm.

The iron arc reference spectrum was made to occupy a portion of the blank space between the cathode and anode zones, corresponding to the Faraday dark space of the discharge under examination, by means of a wedge-shaped diaphragm which served also to blank off all except the dark space section of the discharge image. This reference spectrum was thus obtained without any interference with the spectrograph itself or its plate carrier.

Ilford panchromatic special rapid plates were employed. Developing and fixing were carried out as far as possible under nearly uniform conditions of time of development, concentration and temperature of solutions. The time of all exposures of the discharges, other than that of the iron arc, was two hours. The spectrograms reproduced in Plate 18 were enlarged positives of some of the original negatives obtained.

The gaseous pressure in the discharge vessel was maintained, as a rule, between 40 and 50 mm. Any fall in pressure due to combustion and removal of the product of such combustion was made good from time to time by admission of fresh supplies of gas. The gap width employed throughout was substantially constant at 7.5 to 8 mm. The electrodes were shaped, cleaned and "run in" in the manner previously described in Part I.

The Experimental Results.

The main facts revealed by the spectrograms obtained are summarised in Table I. In the reproductions of the spectrograms, the spectra due to the cathode zones are uppermost, and those of the anode zones and positive columns below, whilst the iron arc reference spectra occupy positions between these.

Spectrograms I, II, IV, V and VI (Plate 18) show nitrogen lines in addition to those enumerated in the two right columns of Table I. These are due to adventitious nitrogen, the amount of which was less than 0.2 per cent., as shown by analyses carried out on a Bone-Newitt gas analysis apparatus.

The CO bands in the spectrograms I to VII are superposed on a faint continuous background which extends from within the visible part of the spectrum to well up into the extreme ultra-violet.

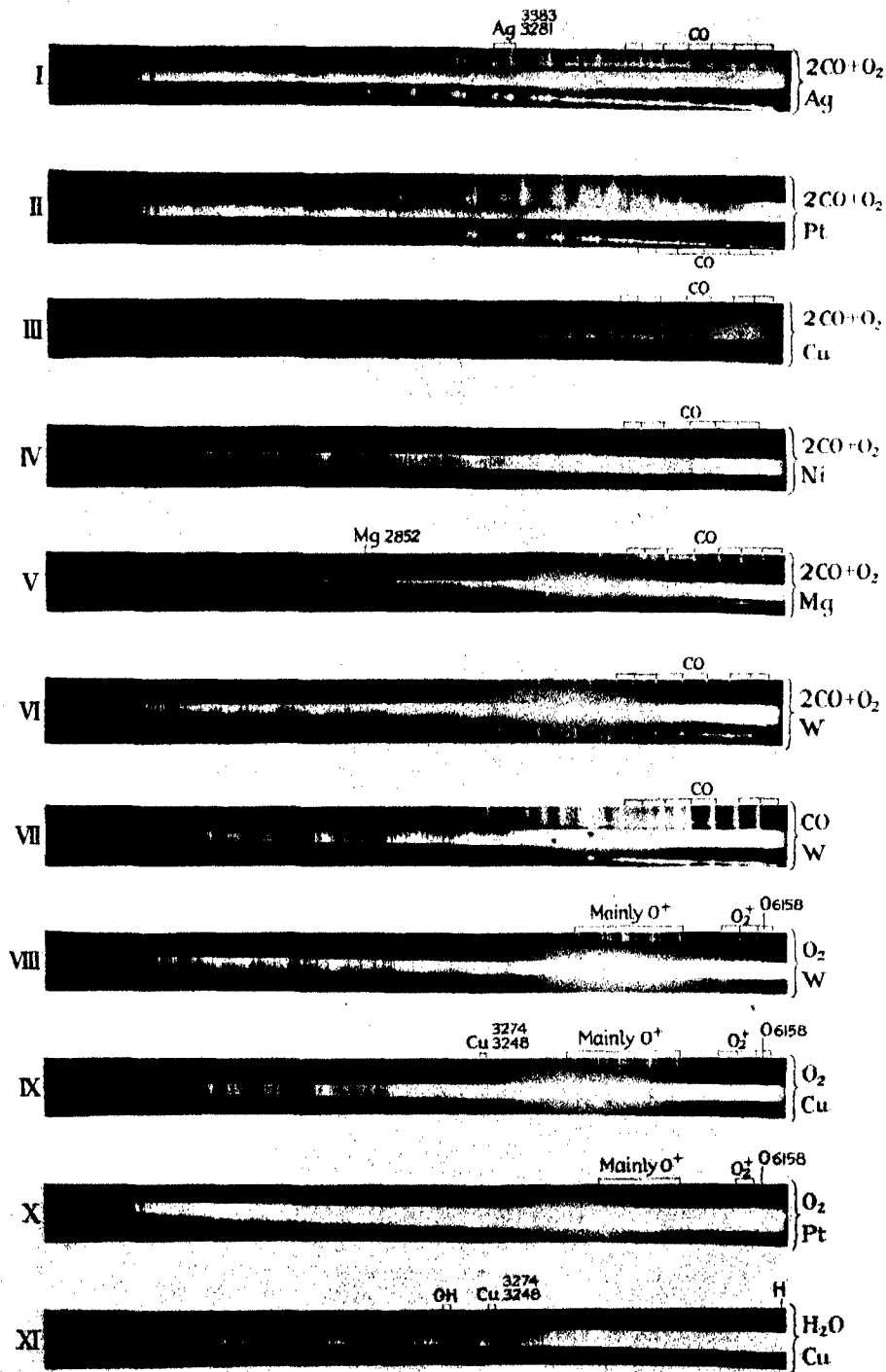


Table I.

Spectro-gram.	Gas.	Elec-trodes.	Gap width in mm.	Average Gas Pressure in mm.	Current in Milli-amps.	Spectrographically Found.	
						In Positive Column.	In Cathode Zone.
I	2 CO + O ₂	Ag	7.0	45	3.0	Ag, very weak; CO bands	Ag, strong; CO bands.
II	2 CO + O ₂	Pt	7.5	45	3.0	No Pt; CO bands	No Pt; CO bands
III	2 CO + O ₂	Cu	7.5	50	2.5	No Cu; CO bands	No Cu; CO bands.
IV	2 CO + O ₂	Ni	8.0	45	3.0	No Ni; CO bands	No Ni; CO bands.
V	2 CO + O ₂	Mg	8.0	60	3.5	Mg very weak, and only in anode spot; CO bands	Mg very weak, and only near cathode surface; CO bands.
VI	2 CO + O ₂	W	7.5	45	3.0	No W; CO bands	No W; CO bands.
VII	CO	W	7.5	40	4.0	No W; CO bands. CN.	No W; CO bands. CN.
VIII	O ₂	W	7.5	35	4.0	Not spectrographed	No W; O ₂ ⁺ , O, O ⁺ .
IX	O ₂	Cu	7.5	35	4.0	Not spectrographed	Cu strong. O ₂ ⁺ , O, O ⁺ .
X	O ₂	Pt	7.5	35	4.0	Not spectrographed	No Pt; O ₂ ⁺ , O, O ⁺ .
XI	H ₂ O	Cu	7.0	15	3.0	Cu very weak, doubtful if present at all; OH strong.	Cu strong; OH strong but weaker than in positive column; H.

Discussion.

The view of the mechanism of the cathodic combustion of "detonating gas," put forward in Parts III and IV postulates the existence of metal atoms within the cathode zone when the cathode material consists of a freely sputtering metal.

The spectrograms afford ample evidence of the presence, as atoms, of sputtered metals. That platinum lines are absent cannot be taken as showing that platinum atoms are themselves absent; it is practically certain that the more characteristic and sensitive platinum lines lie above or below the range covered by the spectrograph employed and do not appear on the present spectrograms for this reason. Spectrogram I affords clear proof of the atomicity of sputtered silver; and it has been shown by Guntherschultze* and by von Hippel and Blechschmidt* that platinum sputters even more readily than does silver in the presence of either carbonic oxide or oxygen. Magnesium, practically speaking, a non-sputtering metal, is faintly visible in Spectrogram V, but only in the immediate vicinity of the anode and cathode

* 'Z. Physik,' vol. 36, p. 563 (1926) and vol. 38, p. 575 (1926); 'Z. Technische Physik,' vol. 8, p. 169 (1927); 'Chem. Zentralblatt,' vol. 2, p. 385 (1927); 'Ann. Physik,' vol. 81, p. 1001 (1926).

surfaces. There is no sign of either nickel (Spectrogram IV) or copper (Spectrogram III) except in the case of the latter in oxygen (Spectrogram IX) and steam (Spectrogram XI). The latter spectrogram reveals also the presence of OH and atomic hydrogen.

The spectrograms in oxygen (Spectrograms VIII, IX and X) show that O_2^+ , O and O^+ are present in the cathode zone. The corresponding lines are absent, however, in the case of "detonating gas." But here again, and for similar reasons as in the case of the absence of platinum lines, this cannot be regarded as evidence of the absence of either O_2^+ , O or O^+ . Thus, for instance, in Spectrogram VII, when the carbonic oxide was contaminated with adventitious nitrogen, cyanogen bands are plainly visible. Further, experiments recently carried out by Mr. Patrick and one of us (G.I.F.) have shown that ozone is always present in the cathodic combustion products of CO — O_2 mixtures.

The spectrograms reveal further, that in no case is carbonic oxide excited to ionisation. Had such ions been present they could not in this case have escaped detection. The various values of c/i (ratio of rate of combustion in cubic centimetres at N.T.P. per minute to the current in milliamperes) observed from time to time whilst obtaining these spectrograms were normal and in accordance with those found in the investigations set forth in Parts III and IV. It follows, therefore, that the cathodic combustion of the "detonating gas" can and does proceed without ionisation of the carbonic oxide.

Summary.

Direct current discharges traversing "detonating gas" and various other gases under experimental conditions similar to those described in Parts III and IV of this series have been spectrographed.

The spectra show, amongst other results, that under these conditions—

- (i) Carbonic oxide molecules are excited but not ionised.
- (ii) The CO-bands in "detonating gas" are superposed on a faint continuous background.
- (iii) Metals are sputtered as atoms.
- (iv) In pure oxygen positively charged oxygen molecule and atom ions, and neutral oxygen atoms are formed; in all probability oxygen atoms are also formed in "detonating gas."

The fact that carbonic oxide is not ionised under the conditions of our

experiments proves that the cathodic combustion of carbonic oxide "detonating gas" is not determined by a prior ionisation of the carbonic oxide.

Our thanks are due to Prof. H. Dingle who interpreted the spectrograms.

One of us (H.H.T.) wishes to thank the Board of Education and the Lord Kitchener National Memorial Fund for grants which enabled him to devote his whole time to this research. We also wish to thank the Government Grants Committee of the Royal Society for a grant with which the cost of some of the apparatus employed in this investigation was defrayed.

The Combination of Nitrogen and Hydrogen Activated by Electrons.

By G. F. BRETT.

(Communicated by A. P. Chattock, F.R.S.—Received July 15, 1930.)

Introduction.

The most recent of several papers on this subject is that of Caress and Rideal*; they give a summary and discussion of the earlier work, and repetition here is unnecessary. Their paper will be taken as the starting point of the present one.

In their experiments a mixture of nitrogen and hydrogen was admitted into a bulb containing a straight wire filament, which formed the axis of a cylindrical grid and anode. The space between these was the reaction space to which electrons of known speed had access from the filament. With electrons of suitable speed, a certain amount of combination took place, and the product, ammonia, was frozen out by surrounding the bulb with liquid air. The resulting fall in pressure, measured by a McLeod gauge, was a measure of the rate of reaction, and the chief part of their work was to examine the rate of reaction as a function of the electronic speeds.

Their chief result was that the rate of reaction increased sharply at two fairly well-defined electron speeds, 17 and 23 volts, which they associated with the known potentials required to produce molecular and atomic ions of nitrogen respectively.

* 'Proc. Roy. Soc.,' A, vol. 115, p. 684 (1927).

The present work was undertaken in order to obtain more accurate values of these critical potentials, and to search for new ones.

Experimental Details.

The experimental method was substantially the same as that of Caress and Rideal; such departures as were made resulted from the following criticism of details in their method.

In the first place, the principle of the method being to measure a pressure change, a McLeod gauge did not seem to be the most satisfactory way, chiefly because it is slow in action and is not, therefore, sufficiently automatic. This is a drawback when numerous readings have to be taken in rapid succession as in the present work. Moreover, it was relative values which were required rather than the absolute values which a McLeod gauge gives, and these are better obtained by other methods.

Second, the use of a tungsten filament is undesirable when hydrogen is present on account of the large amount of thermal dissociation which occurs. The atoms so formed are condensed at surfaces cooled by liquid air, resulting in a change of pressure. When the hydrogen is mixed with nitrogen, and the mixture is activated by electrons from a tungsten filament, the total pressure change is composed, therefore, of two parts: first, that due to the freezing out of ammonia, and, second, that due to dissociation of the hydrogen. This latter is a considerable fraction of the total, and hence the error in measuring the pressure change due to the formation of ammonia may be large. Moreover, some of the atomic hydrogen produced thermally takes part in the reaction, whereas the investigation is concerned with atomic hydrogen only in so far as it is produced by electrons.

The third criticism concerns the fall of potential down the filament, which will affect the sharpness of the breaks in the curve of reaction-rate and electron-volts. Most of the runs in the experiments of Caress and Rideal were made with a straight wire tungsten filament 0.2 mm. in diameter, and as much as 3 cm. in length. It is true that the measured accelerating potentials were applied between the grid and a point having the same potential as the centre of the filament, but it is clear that from a 3 cm. filament there would be quite an appreciable velocity distribution in the electron stream.

In the present work, a Pirani gauge was used instead of a McLeod. The usual commercial pattern was found to be unsatisfactory for a variety of reasons, and it was decided, therefore, to make one specially for these experi-

ments; a design and method of working given by Hughes and Skellett,* seemed to be nearest to what was required. The gauge consisted of 15 mm. of $10\ \mu$ Wollaston wire stretched axially along a small containing tube, and welded at its ends to sealing-in wire. The silver was dissolved away after the mounting was complete; it was found necessary to protect the welds during this process by wax, which was afterwards removed.

The gauge, when in use, was immersed in liquid oxygen, as this was found to be the most convenient way of maintaining a steady zero; it occupied one arm of a Wheatstone bridge operated by a two-volt cell. A suitably shunted moving coil galvanometer with lamp and scale completed the gauge.

The bridge was balanced when the best possible vacuum had been obtained; for any higher pressure the galvanometer spot moved by an amount depending on that pressure, and instead of rebalancing the bridge, the shift of the spot was used as a measure of the pressure.

Incidentally, the small volume (2 c.c.) of the gauge compared with the bulb of a McLeod gave it an additional advantage in sensitivity over the latter, since, for a given volume of the reaction bulb, it is desirable to have the remaining volume (occupied by traps, connecting tubes and gauges) as small as possible.

The second change was to abandon tungsten filaments. Caress and Rideal used occasionally an oxide coated emitter, but they found that with hydrogen alone a large clean-up occurred above 28 volts. Recently, another worker in the same laboratory finds that this does not happen if he uses the special coating preparation of the General Electric Company. This is borne out by the present experiments, throughout which filaments coated with this preparation have been used.

And finally, in order to reduce to a minimum the potential drop down the filament, the coating was applied to an area about 2×2 mm. of platinum foil as thick as the current carrying capacity of the leads would allow—about 8 to 10 amps. The potential drop down the active portion was not much above a quarter of a volt.

At first a commutator was tried with the idea of eliminating entirely the potential drop, but problems of steadiness and reproducibility of the thermionic current led to its abandonment.

For the rest, the experimental arrangement was more or less that of Caress and Rideal, but it is convenient to give here a diagram (fig. 1) of the reaction bulb and the accessories. The grid, of fairly large mesh, was of molybdenum

* 'Phys. Rev.', vol. 30, p. 11 (1927).

wire wound in a flattened form to fit the shape of the foil-emitter, to which it was in close proximity (about 2 mm.). The anode was also of molybdenum.

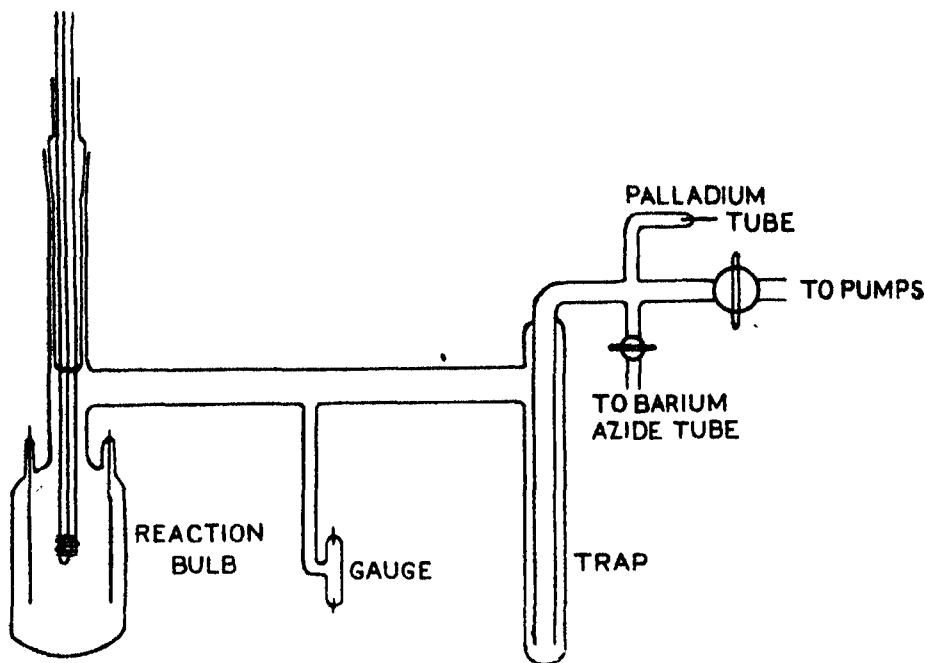


FIG. 1.

Hydrogen was admitted through a palladium tube heated by a flame under such control that any pre-assigned pressure was fairly easily obtained.

Nitrogen was obtained by gentle heating of barium azide, for which thanks are due to the General Electric Company. The water which it contained was driven off by preliminary heating, while the high temperature at which barium carbonate yields carbon dioxide made unimportant the small trace of that substance present in the azide.

No liquid air was used round the reaction bulb; sufficient freezing out of ammonia occurred in the trap and gauge. Incidentally, the liquid air levels at these surfaces changed very slowly, whereas an early test showed that it was difficult to keep a standard level round the reaction bulb without constant attention; it was an advantage, therefore, to be able to dispense here with liquid air.

Procedure.

After setting up the tube, the usual high vacuum technique was employed, including baking the reaction bulb, and heating the metal parts to red heat with an induction furnace.

The next step was to obtain calibration curves for the gauge; these were chiefly for reference purposes, for only relative values of pressure were important. The calibration was made in turn for hydrogen, nitrogen, and a three-to-one mixture of hydrogen and nitrogen, using a McLeod gauge which was afterwards sealed off. The curves were almost linear over quite large ranges.

Preliminary to taking runs, it was found that with the gases taken separately there was some clean-up when the filament was lit and the grid-anode potential was zero. This clean-up varied with time with a new filament, but after prolonged burning of the filament in the gases it became small and constant; with nitrogen, in fact, it became negligible. (This part of the work seemed to indicate that the filament was playing a chemical part as well as supplying electrons, and the results given below should be regarded as subject to this condition. Thus both tungsten and oxide-coated filaments are unsatisfactory from the point of view of the present experiments in that neither acts solely as a source of electrons; and this limitation applies in one way or another to all sufficiently copious emitters.)

When the filament had been "aged" in the manner just indicated, it was possible to start a run with a mixture of the gases. Throughout, a three-to-one hydrogen-nitrogen mixture was used, usually at a pressure of about 0.03 mm. For a given accelerating potential the galvanometer reading of the Pirani gauge was taken every minute for three or four minutes, with a constant thermionic current flowing; the tube was then pumped hard again, a new mixture was introduced at the same pressure as before, and the Pirani readings were taken with a new accelerating potential. This procedure was repeated for a range of voltages from 12 to 30, and later to 40, in half-volt steps. Throughout the thermionic current to the anode was kept constant and at as small a value as was convenient (about 0.2 milliamps.); this was for two reasons. First, to reduce the potential drop down the filament to a minimum; second, to keep the filament temperature low, as by this means the steady clean-up at zero accelerating potential was reduced.

In the four minutes or so during which galvanometer readings were taken, the rate of reaction (in millimetres of galvanometer scale per minute) was

usually uniform, and a curve was drawn connecting it and the corresponding applied potentials. In regions showing sharp rises in the curve the experiments were repeated, this time in quarter-volt steps.

Similar runs were then made with the gases taken separately.

It remained only to correct the voltmeter readings of the applied potentials. This was done with mercury vapour, both by observing the point at which the mercury green line came up, and by a Franck-Hertz experiment.

Results.

1. The separate gases. The rate of change of pressure (in arbitrary units) is shown as a function of the corrected electron-volts in fig. 2, curves (a) and (b), for hydrogen and nitrogen respectively. The hydrogen curve, almost horizontal, requires no comment; the clean-up is small and almost constant. The nitrogen curve, too, is almost horizontal except in the region 16 to 19 volts, where the rise is fairly sharp. The clean-up at all speeds is somewhat less than for hydrogen.

With no applied potential, the clean-up for hydrogen was just over half the value at 16 volts, but for nitrogen it was negligible.

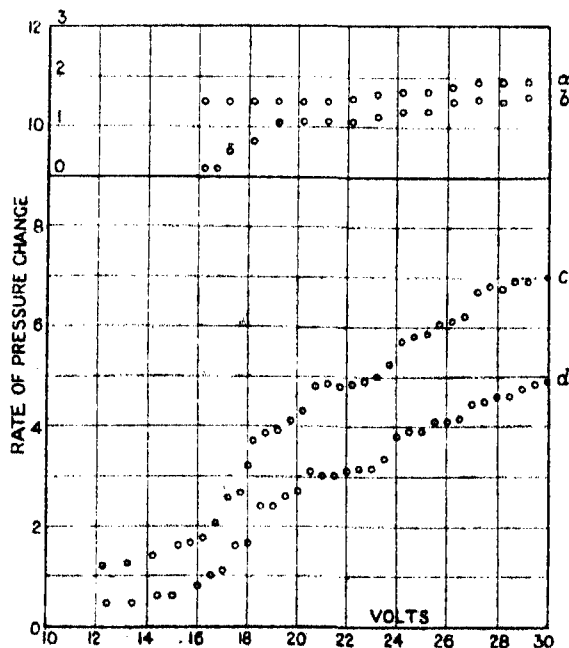


FIG. 2.

2. The 3:1 mixture. Typical curves are shown in fig. 2 (c) and (d). (The ordinates of 2 (c) are displaced a little to display the curves better.) The curves for each break separately are not reproduced here, although the numerical values about to be given are the averages taken from several such sectional curves. Breaks were not always reproducible to the degree of accuracy implied in taking quarter-volt steps, and these values are given, therefore, to the nearest half-volt.

Breaks occurred at 17.0, 18.5, 20.5, 24.5, 27.0 volts, and two diffuse ones at 32-35 and 37-39 volts.

Discussion.

Caress and Rideal obtained breaks in their curves at 17 and 23 volts, and, when a tungsten filament was used, one at 13 volts. Other breaks were simple combinations of these. The 17-volt break was associated with the formation of N_2^+ , and the 23-volt break with N^+ .

Table I shows some of the published values of ionisation and excitation potentials of nitrogen and hydrogen side by side with the potentials at which breaks were obtained in the present work. The values for nitrogen are from a discussion of its heat of dissociation by Mulliken,* and those for hydrogen are from a recent paper by Bleakney.†

Table I.

Observed Breaks (volts).	Critical Potentials.	Nature of Product.
17.0	16.9	N_2^+
18.5	18.0 ± 0.2	$H + H^+$
20.5	20.1	N_2^{+*}
24.5	24.0	$N + N^+$
27.0	26.0	$N' + N^+$
	26 ± 1	$H + H^+$

Of the five chief critical speeds obtained in the present work, two correspond fairly well with the values of Caress and Rideal, the one at 17.0 being associated

* Mulliken, 'Nature,' vol. 122, p. 842 (1928). Turner and Samson, 'Phys. Rev.,' vol. 34, p. 747 (1929), have recently found 15.8 volts for N_2^+ —a volt lower than the value usually accepted. The remaining potentials for nitrogen are likewise lowered by one volt. It seems safer for the time being to take the higher value.

† 'Phys. Rev.,' vol. 35, p. 1180 (1930).

with the formation of molecular ions of nitrogen, and the other at 24·5, with the production of atoms and atomic ions. (Caress and Rideal associated their 23-volt value with atomic ions only.)

Of the three new critical speeds, the value at 18·5 volts seems to correspond to the production of atomic hydrogen, the one at 20·5 volts to the production of an excited state of the nitrogen molecular ion, while the third at 27·0 volts may be associated either with a metastable excited state of the nitrogen atom or with a further production of atomic hydrogen, or with both.

The diffuse breaks seem to be combinations of the sharper ones.

The rate of reaction below the ionisation potential of N_2 is small; this may be accounted for by the fact that the two excited states at 13·0 and 14·8 volts are not metastable. At the pressures used, the time of duration of an excited state is not long enough to make combination likely, and hence only metastable excited states can be regarded as effective. As for the metastable excited state at about 8 volts, the energy available is not enough to produce dissociation, without which combination would not be expected.

The lowest effective electron speed corresponds, therefore, to the production of the ionised molecule of nitrogen at 17 volts. Recent work by Wansborough-Jones* on nitrogen and oxygen also shows that ionisation of the nitrogen is necessary before combination takes place, and it is of interest that in the present work the clean-up of pure nitrogen (fig. 2 (b)) started at about 17 volts.

The break of 20·5 corresponds to an excited state of N_2^+ , which is not metastable, but chemical activity is to be expected because this state goes over, with emission of light, into the normal ionic state N_2^+ . Thus the breaks at 17·0 and 20·5 volts are both to be associated with the activity of the normal ion N_2^+ .

The excited state of the nitrogen atom at about 26 volts is metastable, and hence the observed break at 27 volts may be associated with both nitrogen and hydrogen, in the way indicated in the above table.

It is to be noticed that even below 18·5 volts atomic hydrogen would be present; according to Hughes and Skellett (*loc. cit.*) dissociation begins at about 12 volts. But the curves show that atomic hydrogen and the normal nitrogen molecule do not combine; we may say, therefore, that the most probable mechanism for the ammonia reaction is atomic hydrogen together with one or other of the active states of nitrogen given above.

* 'Proc. Roy. Soc.,' A, vol. 127, p. 511 (1930).

This work was carried out in the H. H. Wills Physical Laboratory, and I wish to thank Prof. A. M. Tyndall for giving me the necessary facilities, and for his interest and advice. I wish also to thank Dr. H. W. B. Skinner who suggested this problem, and gave many helpful suggestions. I am indebted to Dr. G. Herzberg for supplying me with much of the information on nitrogen.

Summary.

The rate of reaction of nitrogen and hydrogen activated by electrons has been measured as a function of the electronic speeds.

The method consisted in measuring the change of pressure produced by freezing out the product of the reaction, a Pirani gauge being used for this purpose.

The rate of reaction was found to rise sharply at the following electronic speeds :—

17·0, 18·5, 20·5, 24·5 and 27·0 volts, corresponding to the production of : N_2^+ , $H + H^+$, N_2^{+*} , $N' + N^+$, $N' + N^+$ and/or $H + H^+$ respectively.*

* I am indebted to Dr. Mulliken for the information that theoretically an excitation potential of the nitrogen molecular ion is to be expected at about a volt above the ionisation potential of the molecule; there is as yet no experimental confirmation of this. The observed break at 18·5 volts in the present work may probably be associated with this excitation potential, as well as with the production of atomic hydrogen.

The λ 3400 Band of Phosphorus Hydride.

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[PLATE 19.]

Introductory.

In the account of the band spectra associated with phosphorus* given in Kayser's "Handbuch der Spectroscopie," mention is made of a band lying between λ 3476 and λ 3379 which was obtained by Geuter† from a discharge tube containing phosphorus and hydrogen.

Reference to the original paper showed that Geuter besides recording the results of an extensive investigation of the spectra produced under various conditions with phosphorus in the flame, in the arc, and in the discharge tube, had also made measurements on this band. The wave-lengths obtained, however, were only considered to be accurate to 0.03 Å. and were quite inadequate for a detailed analysis of the fine structure of the band. It was desirable, therefore, to re-photograph the band under higher dispersion, especially as the experimental data for triplet molecular states are somewhat scanty.

Experimental.

An investigation of the conditions most favourable for the production of the band was first made with the aid of a quartz spectrograph (Hilger's E.2) giving a dispersion varying from 65 Å. per millimetre at λ 5500 to 7.5 Å. per millimetre at λ 2300. Various patterns of discharge tube were tried, that finally adopted‡ is illustrated in fig 1. It is essentially of the H type modified by the introduction of a small bulb with a ground-in stopper between one end of the capillary and the corresponding electrode. The tube was excited by the uncondensed discharge from the secondary of a 4-inch induction coil working on an alternating current supply (50 cycles). The heating of the tube could be controlled to some extent by varying the current through the primary. The current was usually about 3 amperes.

* "Handbuch der Spectroscopie," vol. 6, p. 254.

† 'Z. Wiss. Phot.,' vol. 5, p. 50 (1907).

‡ This type was suggested to the author by Dr. K. R. Rao's work on "Selenium."

This arrangement proved very satisfactory for obtaining the spectrum in the presence of hydrogen. Hydrogen from a commercial cylinder was dried

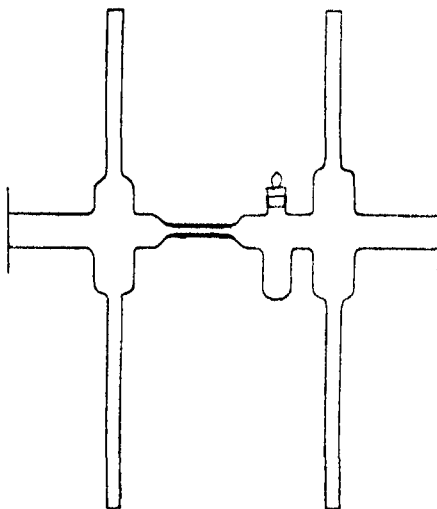


FIG. 1.—Type of discharge tube used in the production of the spectrum of phosphorus hydride.

by passage over P_2O_5 (without this precaution λ 2811 and λ 3064 OH bands appeared) and allowed to pass in a very slow stream through the discharge tube. In passing around the electrode the gas became warmed sufficiently to vaporise a small quantity of phosphorus in the bulb and to carry it into the capillary. With proper adjustment of the primary current and the hydrogen stream no extra heating of the tube was necessary and the transport of phosphorus through the tube was slow and regular. The part of the tube carrying the quartz window at the further end of the capillary was made 2 inches longer than usual and cooled with moist blotting paper. With these precautions to prevent clouding of the window, it was found possible to give an unbroken exposure of several hours. The intensity obtained was such that an exposure of 4 hours was required for a good plate in the second order of the 10-foot grating.

A few experiments were carried out to observe the effect of replacing the hydrogen by various other gases. When the tube was freed as far as possible from all gases other than phosphorus vapour, the very extensive system, stretching from about λ 3500 to beyond λ 2100, which Geuter called "band spectrum C" was present strongly, and is attributed to the molecule P_2 . With the addition of nitrogen no further bands were observed other than those

attributed to N_2 ; but with air, besides the N_2 and NO bands, traces of a system with principal heads at $\lambda\lambda$ 2555, 2478, 2396 and 2320 were obtained. This system was obtained much more strongly with P_2O_5 in copper and magnesium arcs in air, and was identified with the system obtained by Geuter,* de Gramont† and de Wetteville‡ in the arc.

It is clearly a doublet system, which is consistent with its assignment to the molecule PO. Only when hydrogen was present in the tube was the band at λ 3400, which Geuter called "band spectrum B" strongly developed. Under the conditions described earlier in this section this became by far the strongest feature of the spectrum.

Measurements.

The wave-lengths were obtained from measurements on the best of the plates taken in the second order of the grating. Wherever possible the iron standards recommended by the International Astronomical Union§ in 1928 were used for interpolation, but in regions where these were few, the mean values given by Kayser and Konen|| were used. In this region these values, only need reducing by 0.001 Å. to bring them into line with the 1928 values. The dispersion of the grating is 2.7 Å. per millimetre in the second order and lines were resolved down to 0.03 Å. Except in the case of difficult lines the errors in the wave-lengths should not be much greater than 0.005 Å.

The Structure of the Band.

The isolated nature of the band and its widely spaced rotational structure confirm its assignment to a hydride. It resembles the NH band at λ 3360 in having a strong maximum of intensity near the centre and a very symmetrical distribution of lines, with widely spaced series emerging from each extremity. In this case, however, these series appear as doublets instead of triplets. The PH band further differs from the NH band in showing a greater number of secondary maxima of intensity. The central maximum lies at λ 3420, while there are secondary maxima at $\lambda\lambda$ 3427, 3409, 3395 and a sharp edge at λ 3390. The appearance of the band under high dispersion can be seen from the enlargement shown in Plate 19.

Analysis of the band leads to the scheme of energy levels shown in fig. 2.

* 'Z. Wiss. Phot.,' vol. 5, p. 40 (1907).

† 'C. R.,' vol. 149, p. 263 (1909).

‡ 'Z. Wiss. Phot.,' vol. 7, p. 279 (1909).

§ 'Trans. Int. Ast. Union,' vol. 3 (1929).

|| "Handbuch der Spectroscopie," vol. 7, part 1.

which are very close and separated by wider intervals from the upper component. Such structure has been found in the O_2 bands* and is characteristic

* Cf. R. S. Mulliken, 'Phys. Rev.,' vol. 32, p. 880 (1928).

of a $^3\Sigma$ electron level. In the upper state the rotational levels fall into three sets separated by intervals of about 100 cm.^{-1} . Each rotational level consists of two close sub-levels. The whole arrangement of levels is just that to be expected for a $^3\Pi$ state which closely approaches Hund's case *a*. This classification is in harmony with that of the NH band at $\lambda\ 3360$, which has already been assigned to a $^3\Pi \rightarrow ^3\Sigma$ transition.* In the case of the lighter molecule, however, the spin fine structure is of much smaller magnitude and the $^3\Pi$ state tends towards Hund's case *b*, the triplet spacing decreasing rapidly with increasing rotation of the molecule from about 20 cm.^{-1} at the origin. The fine structure of the $^3\Sigma$ levels has not been resolved in the case of NH, but the rotational levels are, of course, more widely spaced. It is from these differences in the relative magnitudes of the spacing of the various energy levels that the differences in the appearance of the two bands arise.

Notation and Term Values.

For the purpose of setting out the various branches and the term values obtained from them, which justify the proposed scheme of energy levels, the full notation recommended in the forthcoming Report on Notation for Spectra of Diatomic Molecules by Mulliken is somewhat cumbersome and in this particular case can be simplified considerably. In the diagram of energy levels the transitions giving rise to the various branches are drawn so that the magnitude of the energy change increases from right to left. It will be seen that from each component Π level the nine transitions which occur group themselves into five branches. These are conveniently called the O, P, Q, R and S branches respectively. Each rotational level of the $^3\Sigma$ state is given in order, a value of *K* starting with 0 for the lowest. The lines denoted by O(*K*), P(*K*), ..., are the members of their respective branches which have the same final rotational level *K*. The O, Q and S branches arise from the upper or A rotational levels of the Π states, while the P and R branches arise from the lower or B rotational levels. The O and S branches are single, the P and R double and the Q triple. The separation in the P(*K*) doublet is equal to that between the first two members of the Q triplet while the separation in the R(*K*) doublet is equal to that between the first and the third. The fact that the separations are equal for equal values of *K* indicates that this fine structure arises in the Σ state. The three components of the rotational levels are distinguished by calling them F_1 , F_2 and F_3 levels such that the O-transitions are

* Cf. R. S. Mulliken, 'Phys. Rev.', vol. 33, p. 730 (1929).

to F_1 levels, the P transitions to F_1 and F_2 levels, and the Q to F_1 , F_2 and F_3 levels. The R transitions are then found to be to F_2 and F_3 levels, and the S transitions to F_3 levels. The lines are distinguished by such symbols as $Q_1(K)$, $Q_2(K)$, ..., etc., according as the transitions are to F_1 , F_2 , ..., levels.

The nine transitions from each of the three component levels $^3\Pi_0$, $^3\Pi_1$ and $^3\Pi_2$ are defined thus :—

$$\begin{aligned} O_1(K) &= F'_A(K-2) - F''_1(K) + T^e + G \\ P_{1,2}(K) &= F'_B(K-1) - F''_{1,2}(K) + T^e + G \\ Q_{1,2,3}(K) &= F'_A(K) - F''_{1,2,3}(K) + T^e + G \\ R_{2,3}(K) &= F'_B(K+1) - F''_{2,3}(K) + T^e + G \\ S_3(K) &= F'_A(K+2) - F''_3(K) + T^e + G. \end{aligned}$$

The F terms represent rotational energy while T^e and G represent amounts of electronic and vibrational energy which are constant for the whole band.

The rotational term differences $\Delta_1 F(K)$ and $\Delta_2 F(K)$ for any energy term F are defined as follows :—

$$\begin{aligned} \Delta_1 F(K) &= F(K+1) - F(K) \\ \Delta_2 F(K) &= F(K+1) - F(K-1). \end{aligned}$$

For the $^3\Pi$ state there are in all six rotational energy functions, viz., F_A and F_B for each of the three component levels. The $\Delta_2 F$ values can be obtained directly from the following line combinations :—

$$\begin{aligned} \Delta_2 F'_A(K) &= Q_1(K+1) - O_1(K+1) = S_3(K-1) - Q_3(K-1), \\ \Delta_2 F'_B(K) &= R_2'(K) - P_2(K). \end{aligned}$$

The values of $\Delta_1 F'(K)$ cannot be determined directly but the following relations hold :—

$$\begin{aligned} \Delta_1 F'_{AB}(K) &= F'_A(K+1) - F'_B(K) = Q_{1,2}(K+1) - P_{1,2}(K+1) \\ &= S_3(K-1) - R_3(K-1). \end{aligned}$$

$$\begin{aligned} \Delta_1 F_{BA}(K) &= F'_B(K+1) - F'_A(K) = P_1(K+2) - O_1(K+2) \\ &= R_{2,3}(K) - Q_{2,3}(K). \end{aligned}$$

If $F_A = F_B$ then $\Delta_1 F_{AB}(K) = \Delta_1 F_{BA}(K)$ otherwise

$$\frac{1}{2}[\Delta_1 F_{AB}(K) - \Delta_1 F_{BA}(K)] = \frac{1}{2}[F_A(K+1) + F_A(K)] \\ - \frac{1}{2}[F_B(K+1) + F_B(K)].$$

This quantity which may be called $\delta_{AB}(K)$ may then be taken as a measure of the magnitude of the AB doubling.

For the final $^3\Sigma$ level there are three rotational energy functions $F''_{1,2,3}$. The $\Delta_2 F''(K)$ values are obtained from the relations:—

$$\Delta_2 F''_1(K) = Q_1(K-1) - O_1(K+1)$$

$$\Delta_2 F''_2(K) = R_2(K-1) - P_2(K+1)$$

$$\Delta_2 F''_3(K) = S_3(K-1) - Q_3(K+1).$$

The three sets of O, P, Q, R and S branches yield three values of each of these quantities which should agree. The $\Delta_1 F(K)$ values have not been evaluated as they have no special significance.

The term differences obtained according to the above equations are set out in Tables I to VIII.

Table VIII.—Mean Values of $\delta_{AB}(K)$.

K.	$^3\Pi_1 \rightarrow ^3\Sigma.$	$^3\Pi_1 \rightarrow ^3\Sigma.$	$^3\Pi_0 \rightarrow ^3\Sigma.$
0			
1		0.12	0.11
2	0.16	0.38	0.13
3	—	0.58	-0.06
4	0.21	0.64	0.02
5	0.42	0.73	-0.23
6	0.46	1.06	0.19
7	0.72	1.18	0.01
8	0.83	1.14	-0.47
9	1.00	1.24	-0.41
10	1.29	1.05	-0.19

Table I.— $^3\Pi_2 \rightarrow ^3\Sigma$ Branches.

K	O _r	P _r	P _r	Q _r	Q _r	Q _r	R _r	R _r	S _r
0									
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									

Note to Table I.—The figures in brackets after the wave-numbers represent the intensities of the lines. It will be seen that O_r and Q_r are very weak branches while P_r is rather weak.

† Indicates that the intensity is affected by blending with another line.

d Indicates that the line appeared rather wide, probably an unresolved pair.

Table II.— $^3\Pi_1 \rightarrow ^3\Sigma$ Branches.

K.	O_1	P_1	P_2	P_1	Q_1	Q_2	Q_3	R_1	R_2	S_1
0			29288.35 (11†)	29290.16 (3)	29321.85 (3)	29323.08 (2d)	29322.43 (6)	29352.84 (2†)	29340.19 (5)	29372.36 (11†)
1			269.32 (0)	271.52 (13†)	319.61 (0)	321.85 (3)	318.78 (11†)	366.98 (11)	355.13 (11)	402.51 (6)
2	240.13 (2)		249.14 (2)	251.24 (12†)	316.53 (2)	318.75 (10d)	314.75 (10d)	379.40 (3)	368.85 (10)	432.30 (8)
3	204.25 (2)		238.33 (9)	230.30 (2)	312.48 (7)	314.75 (10d)	314.75 (10d)	391.08 (7)	381.64 (11)	460.99 (11†)
4	167.42 (4)		206.86 (12d)	206.70 (12d)	307.57 (8)	309.87 (7)	310.11 (7)	402.08 (11†)	393.46 (11)	488.94 (8)
5	129.98 (8†)		184.30 (7)	186.15 (9)	301.92 (7)	303.84 (5)	304.57 (5)	412.13 (8)	404.52 (11)	515.73 (7)
6	091.68 (4)		161.35 (6)	163.01 (7)	295.54 (11)	297.42 (4)	297.95 (12d)	421.45 (8)	414.74 (10)	541.86 (5)
7	052.80 (4)		137.61 (6)	139.20 (6)	288.35 (11)	290.16 (3)	290.92 (11)	429.93 (7)	424.13 (11)	566.91 (5†)
8	29013.56 (8d)		113.25 (5)	114.90 (3)	280.28 (6)	281.99 (2)	283.18 (3)	437.38 (4)	432.50 (8)	590.87 (2)
9	28973.23 (3)		088.21 (4)	089.63 (3)	271.52 (13†)	273.22 (4†)	274.39 (1)	443.94 (11†)	440.24 (3)	613.83 (1)
10	932.53 (3)		062.41 (3)	063.88 (0)	261.75 (7)	263.15 (1)	264.71 (1)		447.69 (0)	635.64 (1)
11	891.33 (1)		035.79 (4)	037.10 (1)	251.24 (12)	252.22 (0)	254.04 (0)			654.96 (1)
12	849.30 (0)		29008.46 (3)	29008.64 (1)	240.13 (2)					
13	806.72 (0)		28980.11 (2)	28981.17 (1)						
14	763.33 (-1)		950.79 (1)	951.83 (0)						
15										
16										

† Indicates that the intensity is affected by superposition of another line.

d Indicates that the line appeared rather wide, probably an unresolved pair.

Table III.— $^3\Pi_0 \rightarrow ^5\Sigma$ Branches.

K.	O _r	P _r	P _r	Q _r	Q _r	Q _r	R _r	R _r	S _r
0		29425.46 (5)		29443.94 (11†)	29445.82 (2)	29445.82 (2)	29459.36 (1)	29462.16 (3)	29488.50 (−1)
1	29394.91 (2)	410.02 (6)	29428.29 (2)	446.36 (10)	449.39 (1)	449.39 (1)	479.36 (7†)	481.83 (3†)	535.97 (0)
2	362.09 (3)	396.82 (8)	412.69 (4)	449.93 (11)	452.30 (8)	452.30 (8†)	500.24 (5)	502.49 (5)	574.03 (0)
3	330.95 (4)	382.74 (8)	398.26 (8)	454.14 (11)	456.40 (7)	456.40 (7†)	521.45 (5)	523.70 (3)	612.38 (−1)
4	300.83 (5)	370.32 (5)	384.88 (10)	458.96 (10)	460.99 (11†)	460.99 (11†)	542.85 (5)	545.21 (2)	
5	271.87 (4†)	358.45 (4)	372.36 (11†)	463.87 (8)	465.84 (8)	465.84 (8)	564.64 (5)	566.91 (5†)	
6	243.08 (10)	346.88 (4)	360.38 (12)	468.83 (6)	470.59 (7)	470.59 (7)	586.08 (4)	588.73 (0)	
7	214.76 (6)	335.37 (3)	348.73 (12)	473.48 (6)	475.12 (8)	475.12 (8)	607.39 (2)	610.06 (−1)	
8	186.54 (9)	323.68 (34d)	336.99 (6)	477.73 (4)	479.36 (7†)	479.36 (7†)	628.03 (2)		
9	158.43 (12d)	311.52 (2)	325.18 (8)	481.65 (3†)	483.05 (6)	483.05 (6)	648.17 (1)		
10	129.98 (8)		313.01 (7)	484.56 (2)	486.03 (4)	486.03 (4)			
11	101.55 (12†)		300.53 (5)	488.18 (3)	488.84 (8†)	488.84 (8†)			
12	072.22 (8)		287.27 (4)						
13	043.84 (4)								
14	013.56 (8d)								
15									

Note to Table III.—The branch S₂ can be seen from the intensities given to be very weak, while R₂ is also rather weak. The very weak branch Q₃ was difficult to observe on account of overlapping of the other very strong Q branches.

† Indicates that the intensity is affected by superposition of another line.

d Indicates that the line appeared rather wide, probably an unresolved pair.

Table V.—Rotational Term Differences for $^3\Pi_1$ State.

K.	$\Delta F_{\text{ma}}(K)$ $P_1(K+2)$ $-O_1(K+2)$	$\Delta F_{\text{ab}}(K)$ $Q_1(K+1)$ $-P_1(K+1)$	$\Delta F_{\text{a}}(K)$ $Q_1(K+1)$ $-O_1(K+1)$	$\Delta F_{\text{ba}}(K)$ $R_2(K)$ $-Q_2(K)$	$\Delta F_{\text{b}}(K)$ $R_2(K)$ $-P_2(K)$	$\Delta F_{\text{ab}}(K)$ $S_2(K-1)$ $-R_2(K-1)$	$\Delta F_{\text{a}}(K)$ $S_2(K-1)$ $-Q_2(K-1)$
0							
1	31.39	31.39	31.26	30.99	78.63	32.17	
2	46.99	47.26	47.21	47.37	110.08	47.38	
3	63.88	63.51	63.34	63.83	141.94	63.45	109.87
4	78.72	79.37	79.24	78.60	173.75	78.35	142.21
5	94.47	95.14	95.05	94.51	205.27	95.38	174.09
6	110.21	111.27	111.24	110.22	237.15	111.26	205.67
7	125.64	127.15	127.00	125.91	268.58	127.12	237.29
8	141.67	142.79	142.67	141.53	299.77	142.78	268.96
9	157.09	158.32	158.27	157.10	330.69	158.37	299.95
10	172.55	173.53	173.54	172.42		173.59	330.65
11	187.80	188.34	188.83			188.95	361.25
12	202.92		204.34				390.25
13	217.84						

Table VI.—Rotational Term Differences for $^3\Pi_0$ State.

K.	$\frac{\Delta_1 F'_{3A}(K)}{P_1(K+2)}$ $-O_1(K+2)$	$\frac{\Delta_1 F'_{AB}(K)}{Q_1(K+1)}$ $-P_1(K+1)$	$\frac{\Delta_1 F'_A(K)}{Q_1(K+1)}$ $-O_1(K+1)$	$\frac{\Delta_1 F'_{3A}(K)}{R_3(K)}$ $-Q_3(K)$	$\frac{\Delta_1 F'_B(K)}{R_3(K)}$ $-P_3(K)$	$\frac{\Delta_1 F'_{3A}(K)}{R_3(K)}$ $-Q_3(K)$	$\frac{\Delta_1 F'_{AB}(K)}{S_3(K-1)}$ $-R_3(K-1)$	$\frac{\Delta_1 F'_A(K)}{S_3(K-1)}$ $-Q_3(K-1)$
0	17.78	17.53	54.48	36.43	53.90	36.01	36.34	125.45
1	36.17	36.70	90.21	53.96	90.32	53.91	54.14	160.08
2	53.93	54.04	125.45	71.52	125.63	71.40	71.54	
3	71.53	71.52	160.16	88.71	160.11	88.81	88.68	
4	88.51	88.63	193.97	105.42	194.32	—	—	
5	105.65	105.46	227.51	123.21	227.63	122.57		
6	122.23	121.86	260.36	138.56	260.50			
7	138.64	138.13	292.82	154.58	292.66			
8	154.59	154.18	324.63	170.44	324.49			
9	170.55	170.04	356.05					
10	186.72	185.53	387.29					
11		200.57	417.27					
12								

Table VII.—Rotational Term Differences for $^3\Sigma$ State.

K.	$^3\Pi_2 - ^3\Sigma.$			$^3\Pi_1 - ^3\Sigma.$			$^3\Pi_0 - ^3\Sigma.$		
	$\frac{\Delta F_1''(K)}{Q_1(K-1)}$ $-O_1(K+1)$	$\frac{\Delta F_2''(K)}{R_2(K-1)}$ $-P_2(K+1)$	$\frac{\Delta F_3''(K)}{S_3(K-1)}$ $-Q_3(K+1)$	$\frac{\Delta F_1''(K)}{Q_1(K-1)}$ $-O_1(K+1)$	$\frac{\Delta F_2''(K)}{R_2(K-1)}$ $-P_2(K+1)$	$\frac{\Delta F_3''(K)}{S_3(K-1)}$ $-Q_3(K+1)$	$\frac{\Delta F_1''(K)}{Q_1(K-1)}$ $-O_1(K+1)$	$\frac{\Delta F_2''(K)}{R_2(K-1)}$ $-P_2(K+1)$	$\frac{\Delta F_3''(K)}{S_3(K-1)}$ $-Q_3(K+1)$
0			50.00			49.93			49.92
1			83.71			83.73			83.54
2			117.56			117.55			117.63
3			150.93			150.88			151.13
4			184.49			184.27			184.40
5			217.62			217.83			217.75
6			250.75			250.94			250.71
7			283.63			283.73			283.71
8			316.52			316.48			316.51
9			349.09			349.12			349.38
10			381.54			381.60			381.50
11			413.53						
12			445.46						
13									

Table VIII.—(See p. 334.)

Discussion of the Electron States.

In the following discussion of the electron states involved in the emission of the PH band the notation used is as far as possible in accordance with that recently agreed upon by band spectroscopists.* Also, in order not to burden this paper, which deals with a particular case, with too much material of a general nature, it is assumed that the reader is familiar both with this notation and with the general theory of molecular energy levels. For further details on these matters the references given above should be consulted.

The Final State.

The structure of the band in respect of number of branches, their spacing and intensity distribution, is that associated with a transition between ${}^3\Pi$ and ${}^3\Sigma$ terms while the nature and magnitude of the fine structure and the form of the rotational term differences appearing in the final state show that it is of the ${}^3\Sigma$ -type. In ${}^3\Sigma$ states the energy equation to be expected is a slightly modified form of that for Hund's case *b* multiplet states. In case *b* states the resultant spin electronic angular momentum *S* is coupled to the axis of the angular momentum *K* which is the resultant of *Λ*, the component of orbital angular momentum along the electric axis, and *O*, the total angular momentum perpendicular to the axis. This gives the quantum number *J* representing the resultant angular momentum of the molecule, and whose possible values are

$$J = K + S, \quad K + S - 1, \quad \dots \quad |K - S|,$$

where the values of *K* are given by

$$K = |\Lambda|, \quad |\Lambda| + 1, \quad |\Lambda| + 2, \dots$$

For a ${}^3\Sigma$ state as here considered $\Lambda = 0$ and $S = 1$ so that *K* has all integral values starting from 0, and for each value of *K* there are three values of $J = K, K \pm 1$.

* The substance of this agreement is shortly to be published in an article in the 'Physical Review' by R. S. Mulliken, "Report on Notation for Spectra of Diatomic Molecules." An account which needs only slight revision is also given by R. S. Mulliken in 'Review of Modern Physics,' vol. 2, No. 1, p. 60 (1930). A preliminary account appeared in the "Discussion on Molecular Spectra," 'Faraday Society Trans.,' pp. 628-633, 770-772, and Errata (September, 1929); also in book form (Gurney and Jackson, 1930).

The general term value given by Mulliken* for case *b* after omission of a term in Λ is

$$T = T^* + G + B_v [K(K+1) + \bar{G}^2] + f(K, J - K) + \phi(K, J) + D_v K^2 (K+1)^2.$$

In this equation T^* is constant for a given electronic state and represents the electronic energy; G is constant for a given state of vibration in the electronic state and represents vibrational energy. This must not be confused with $\bar{G}^2$ within the bracket which represents the contribution to the rotational energy of a rapidly varying component of electronic angular momentum perpendicular to the electric axis. It is of no practical importance, as it cannot be separated in the analysis from T^* and G . The part

$$F = B_v [K(K+1)] + D_v K^2 (K+1)^2$$

represents the rotational energy of the molecule as a function of K . B_v and D_v are constants for a given value of the vibrational quantum number v . The small term $\phi(K, J)$ arises from interaction between the electronic angular momentum G and the nuclear rotation. Its usual effect is to cause a slight change in the value of B_v or to make K depart slightly from integral values. The remaining term $f(K, J - K)$ represents the interaction of the spin S with the rest of the molecule which gives rise to the three components F_1 , F_2 and F_3 for each value of K in the rotational term. The subscripts are added so that for F_1 , F_2 , F_3 , the resultant $J = K + S$, K , $K - S$, where $S = 1$, that is so that $J - K = 1, 0, -1$. The interaction of S with the small magnetic field developed parallel to K gives rise to a term†

$$\gamma/2 \{J(J+1) - K(K+1) - S(S+1)\}.$$

In addition to this Kramers‡ has shown that there is an energy of interaction $w(K, J - K)$ of the individual spins which make up the resultant S when this is greater than $\frac{1}{2}$. For $^3\Sigma$ states he obtains:—

$$w(K, +1) = -\epsilon [1 - 3/(2K+3)]; \quad w(K, 0) = +2\epsilon; \\ w(K, -1) = -\epsilon [1 + 3/(2K+1)].$$

* 'Reviews of Modern Physics,' vol. 2, p. 106 (1930). The notation used in the present paper differs slightly from Mulliken's in accordance with the more recent recommendations of the Report.

† Cf. E. C. Kemble, "Molecular Spectra in Gases," pp. 345-347, 'Bulletin Nat. Res. Council U.S.,' No. 57; also J. H. van Vleck, 'Phys. Rev.,' vol. 33, pp. 498-500 (1929).

‡ 'Z. Physik,' vol. 53, p. 422 (1929).

Combining this with the above term

$$f(K, +1) = \gamma K - \epsilon [1 - 3/(2K + 3)]; \quad f(K, 0) = -\gamma + 2\epsilon;$$

$$f(K, -1) = -\gamma(K + 1) - \epsilon [1 + 3/(2K + 1)].$$

It will be noticed from these expressions that the behaviour of the term in ϵ is quite different from that in γ with increasing value of K . In the former, the states with $J = K \pm 1$ form a narrow doublet whose separation decreases with increasing K and whose centre is separated from the state $J = K$ by the approximately constant interval 3ϵ . In the latter the states with $J = K \pm 1$ diverge from the state with $J = K$ by the increasing amounts $\gamma(K + 1)$, $-\gamma K$. Turning to the experimental data for PH it is observed that the state $J = K$ is well separated from the $J = K \pm 1$ states, and also that these latter states show increasing separation with K . The actual separations can be well represented by the above formulæ using the values

$$\epsilon = 2.14, \quad \gamma = -0.072.$$

In fig. 3 the curves are plotted from these values while the points represent the observed separations.

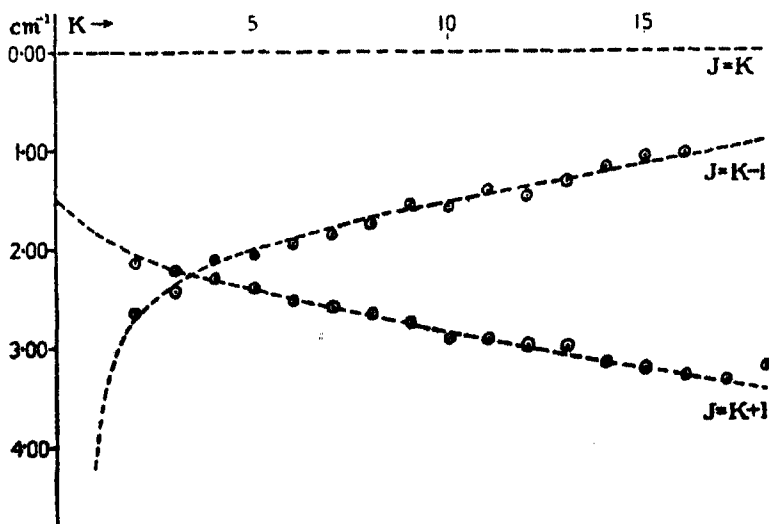


FIG. 3.—Comparison of the observed and calculated values of the fine structure triplet separations in the $^2\Sigma$ level of the λ 3400 band of PH. The curves represent the separations calculated from the formulæ $f(K, +1) = \gamma K - \epsilon [1 - 3/(2K + 3)]$; $f(K, 0) = -\gamma + 2\epsilon$; $f(K, -1) = -\gamma(K + 1) - \epsilon [1 + 3/(2K + 1)]$, $f(K, 0)$ being taken as axis of reference. The points represent the observed values. In the above formulæ the values obtained for the constants were $\epsilon = 2.14 \text{ cm.}^{-1}$, $\gamma = -0.072 \text{ cm.}^{-1}$.

The rotational term differences for the $^3\Sigma$ state are well represented by the following values of the rotational constants

$$B_0'' = 8.411 \text{ cm.}^{-1} \quad D_0'' = 4.28 \times 10^{-4} \text{ cm.}^{-1}$$

whence

$$I_0'' = 3.293 \times 10^{-40} \text{ gm./cm.}^2 \quad r_0'' = 2.06 \times 10^{-8} \text{ cm.}$$

since the λ 3400 band is the only one observed no direct value of ω_0'' has been obtained. The well-known relation

$$D_0 = 4B_0^3/\omega_0^2$$

however leads to the value $\omega_0'' = 2380 \text{ cm.}^{-1}$.

The Initial State.

The initial electron state shows three sets of rotational levels separated by intervals of about 100 cm.^{-1} . For a compound of the molecular weight of PH such large spacing is only to be expected for a $^3\Pi$ state. The form of the rotational term differences suggests that this level is an example of Hund's case *a*. In case *a* the spin *S* is quantised with reference to the electric axis, on account of the magnetic field along this axis produced by Λ . This gives rise to a quantum number Σ which takes the values $-S, -S+1, \dots S$. This quantum number is then combined with Λ to give a resultant $\Omega = |\Lambda + \Sigma|$, which combined with 0 forms the resultant angular momentum of the molecule represented by the quantum number *J*. This takes the values

$$J = \Omega, \quad \Omega + 1, \quad \Omega + 2, \dots$$

For a triplet level $S = 1$ so that there are three values of Ω , viz., 0, 1 and 2. The energy term for this case is

$$T = T^* + G + A\Lambda\Sigma + B_v[J(J+1) - \Omega^2 + \bar{G}^2 + S_{\text{perp.}}^2] \\ + \phi_i(\Sigma, J) + D_v J^2(J+1)^2.$$

Here different values of Σ in the term $A\Lambda\Sigma$ give the different components of the molecular electronic multiplet. The term $\phi_i(\Sigma, J)$ has two values ϕ_A and ϕ_B for each value of Σ and *J* and gives rise to the so-called Λ -type doubling of each of the rotational levels. These two components are the A and B levels of the previous sections. The magnitude of the doublet separations are indicated by Table VIII.

Approximate values of B_v' for this state have been calculated as follows. It is assumed that D_v' will be about $4.0 \times 10^{-4} \text{ cm.}^{-1}$. The amount

$D[(K+1)^2(K+2)^2 - K^2(K-1)^2]$ is then added to the values of $\Delta_2 F(K)$ from Tables IV to VI, and the sums divided by $4(K + \frac{1}{2})$. This procedure leads to the values given in Table IX.

Table IX.—Rotational Constant B for $^3\Pi$ Level.

K.	$^3\Pi_0$.	$^3\Pi_1$.	$^3\Pi_2$.
1	9.08		
2	9.03	7.87	
3	8.96	7.90	7.19
4	8.92	7.92	7.27
5	8.76	7.92	7.26
6	8.79	7.96	7.30
7	8.73	7.96	7.34
8	8.67	7.96	7.37
9	8.62	7.97	7.40
10	8.57	7.95	7.43

The results show that B depends very considerably upon the value of Σ . Further, while the values obtained for the $^3\Pi_1$ levels are very nearly constant, as they should be, the values for the $^3\Pi_0$ levels decrease, and the values for the $^3\Pi_2$ levels increase, with K. This probably indicates that the $^3\Pi$ state is not completely case *a* but tends toward case *b*.

The values of Ω (0, 1, 2) have been assigned to the levels under the assumption that the $^3\Pi$ level here occurring is inverted. This is justified by examination of the first lines of each branch. For $\Omega = 2$ the only line with $K = 0$ should be $S_3(0)$; for $\Omega = 1$ there should be $S_3(0)$, $R_2(0)$ and $R_3(0)$, while for $\Omega = 0$ the lines $Q_2(0)$ and $Q_3(0)$ should also appear. For $K = 1$ additional lines should appear thus: for $\Omega = 2$, $R_2(1)$ and $R_3(1)$; for $\Omega = 1$; $Q_1(1)$, $Q_2(1)$ and $Q_3(1)$; and for $\Omega = 0$, $P_1(1)$ and $P_2(1)$. Not all of these lines have been observed owing to overlapping with other lines or to their low intensity, but sufficient of them have been found to establish the assignment of Ω as may be seen from Tables I to III.

The magnitude of the constant A in the term $A\Lambda\Sigma$ can be obtained from the early members of the branches by using the expression for the energy term given above, neglecting the small factors this is

$$T = \text{const.} + A\Lambda\Sigma + B[J(J+1) - \Omega^2] + \dots$$

The lowest values of this are, omitting the constant :—

J.	${}^3\Pi_0$	${}^3\Pi_1$	${}^3\Pi_2$
0	— A		
1	— A + 2B	0 + B	
2	— A + 6B	0 + 5B	A + 2B
3	— A + 12B	0 + 11B	A + 6B

From this table it is seen that

$${}^3\Pi_2(2) - {}^3\Pi_1(1) = {}^3\Pi_1(1) - {}^3\Pi_0(0) = A + B,$$

so that by subtracting the appropriate value of B from differences between the wave-numbers of lines originating in transitions from the above levels to a common final level the value of A may be determined. A similar process may be carried out for higher members. In this way it is found that for

$${}^3\Pi_2 \rightarrow {}^3\Pi_1 \dots A = -121 \text{ cm.}^{-1}$$

$${}^3\Pi_1 \rightarrow {}^3\Pi_0 \dots A = -111 \text{ cm.}^{-1}.$$

The discrepancy would appear to indicate the necessity for a further term in Σ , probably as a result of a tendency toward case *b*.

Notation.

In the simplified notation used here stress has been laid on the value of K and O, P, Q, R, S have been used to indicate $\Delta K = 2, 1, 0, -1, -2$. In the full notation these letters are used to indicate these values of ΔJ , the value of ΔK being indicated by a similar letter placed as a superscript. Also instead of K being placed in brackets after the main symbol the value of J is usually indicated. For a comparison of the two notations the symbols for the transitions shown in the energy level diagram are given in a table below.

Table X.—Comparison of Notations.

Simplified notation.	Full Notation.		
	${}^3\Pi_1 \rightarrow {}^3\Sigma$	${}^3\Pi_1 \rightarrow {}^3\Sigma$	${}^3\Pi_0 \rightarrow {}^3\Sigma$
$O_1(6)$	${}^OP_{1A1}(5)$	${}^OP_{2A1}(5)$	${}^OP_{2A1}(5)$
$P_1(6)$	${}^PQ_{1B1}(5)$	${}^PQ_{1B1}(5)$	${}^PQ_{2B1}(5)$
$P_2(6)$	${}^PQ_{1B2}(6)$	${}^PQ_{2B2}(6)$	${}^PQ_{2B2}(6)$
$Q_1(6)$	${}^QR_{1A1}(5)$	${}^QR_{2A1}(5)$	${}^QR_{2A1}(5)$
$Q_2(6)$	${}^QR_{1A2}(6)$	${}^QR_{2A2}(6)$	${}^QR_{2A2}(6)$
$Q_3(6)$	${}^QP_{1A3}(7)$	${}^QP_{2A3}(7)$	${}^QP_{2A3}(7)$
$R_1(6)$	${}^RR_{1B1}(6)$	${}^RR_{2B1}(6)$	${}^RR_{2B1}(6)$
$R_2(6)$	${}^RR_{1B2}(7)$	${}^RR_{2B2}(7)$	${}^RR_{2B2}(7)$
$S_2(6)$	${}^SR_{1A3}(7)$	${}^SR_{2A3}(7)$	${}^SR_{2A3}(7)$

Catalogue of Lines of PH.

Table XI contains a general catalogue of the wave-lengths measured in the λ 3400 band of PH. The corresponding intensities, wave-numbers and classification in terms of the simplified notation are given in the second, third and fourth columns.

Table XI.—Catalogue of Wave-lengths.

λ (Å.).	i .	ν .	Classification.		
			$^1\Pi_2 - ^3\Sigma$.	$^3\Pi_1 - ^3\Sigma$.	$^3\Pi_0 - ^3\Sigma$.
3371.152	1	29654.96		$S_2(11)$	
71.924	1	648.17	$R_2(9)$		
73.350	1	635.64		$S_2(10)$	
74.216	2	628.03	$R_2(8)$		
75.835	1	613.83		$S_2(9)$	
75.999	-1	612.38	$S_2(3)$		
76.264	-1	610.06	$R_2(7)$		
76.569	2	607.39	$R_2(7)$		
78.454	2	590.87		$S_2(8)$	
78.698	0	588.73	$R_2(6)$		
79.001	4	586.08	$R_2(6)$		
80.378	0	574.03	$S_2(2)$		
81.192	5	566.91	$R_2(5)$	$S_2(7)$	
81.452	5	564.64	$R_2(5)$		
83.674	2	545.21	$R_2(4)$		
83.946	5	542.85	$R_2(4)$		
84.059	5	541.86		$S_2(6)$	
84.734	0	535.97	$S_2(1)$		
86.140	3	523.70	$R_2(3)$		
86.398	5	521.45	$R_2(3)$		
87.041	7	515.78		$S_2(5)$	
88.576	5	502.49	$R_2(2)$		
88.822	5	500.34	$R_2(2)$		
89.024	-1	498.50	$S_2(0)$		
90.069	2	489.49	$Q_1(13)$		
90.143	8	488.84	$Q_1(12)$	$S_2(4)$	
90.220	3	488.18	$Q_2(12)$		
90.382	2	486.77			
90.467	4	486.03	$Q_1(11)$		
90.638	2	484.76	$Q_2(11)$		
90.809	6	483.05	$Q_1(10)$		
90.950	3	481.83	$R_2(1)$		
90.971	3	481.65	$Q_2(10)$		
91.186	3	479.78			
91.235	7	479.36	$R_2(1)$		
91.421	4	477.73	$Q_2(9)$		
91.722	8	475.12	$Q_1(8)$		
91.914	6	473.45	$Q_2(8)$		
92.244	7	470.59	$Q_1(7)$		
92.445	6	468.83	$Q_1(7)$		
92.753	0	466.16	$Q_2(6)$		
92.790	8	465.84	$Q_1(6)$		
93.017	8	463.87	$Q_2(6)$		
93.214	3	462.16	$R_2(0); Q_2(5)$		
93.349	11	460.99	$Q_1(5)$	$S_2(3)$	
93.439	0	460.20			

Table XI—(continued).

λ (I.A.).	i .	ν .	Classification.		
			$^3\Pi_2 - ^3\Sigma$.	$^3\Pi_1 - ^3\Sigma$.	$^3\Pi_0 - ^3\Sigma$.
3393.536	1	29459.36	$R_2(0)$		
93.583	10	458.95	$Q_2(5)$		
93.776	2	457.28			
93.877	7	456.40	$Q_2(4); Q_2(4)$		
94.137	11	454.14	$Q_2(4)$		
94.350	8	452.30	$Q_2(3); Q_2(3)$		
94.624	11	449.93	$Q_2(3)$		
94.685	1	449.39			
94.778	1	448.58	$Q_2(2); Q_2(2)$		
94.881	0	447.69		$R_2(10)$	
94.979	2	446.84			
95.032	10	446.38	$Q_2(2)$		
95.096	2	445.82	$Q_2(1); Q_2(1)$		
95.314	11	443.94	$Q_2(1)$	$R_2(10)$	
95.740	3	440.24		$R_2(9)$	
96.070	4	437.38		$R_2(9)$	
96.632	8	432.50		$R_2(8)$	$S_2(17); S_2(16)$
96.656	8	432.30		$S_2(2)$	
96.795	2	431.10			$S_2(18); S_2(15)$
96.929	7	429.93		$R_2(8)$	
97.119	2	428.29	$P_2(1)$		$S_2(14)$
97.446	5	425.46	$P_2(1)$		
97.599	11	424.13		$R_2(7)$	$S_2(13)$
97.908	8	421.45		$R_2(7)$	
98.296	3	418.10			$S_2(12)$
98.684	10	414.74		$R_2(6)$	
98.921	4	412.69	$P_2(2)$		
98.986	8	412.13		$R_2(6)$	
99.149	6	410.72			$S_2(11)$
99.229	6	410.02	$P_2(2)$		
99.865	11	404.52		$R_2(5)$	
3400.098	6	402.51		$S_2(1)$	
00.148	11	402.08		$R_2(5)$	$S_2(10)$
00.590	8	398.26	$P_2(3)$		
00.872	8	395.82	$P_2(3)$		
00.989	2	394.91	$O_2(2)$		
01.145	11	393.46		$R_2(4)$	
01.337	10	391.80			$S_2(9)$
01.420	7	391.08		$R_2(4)$	
02.139	10	384.88	$P_2(4)$		
02.386	8	382.74	$P_2(4)$		
02.513	11	381.64		$R_2(3)$	
02.680	11	380.20			$S_2(8)$
02.773	3	379.40		$R_2(3)$	
03.588	11	372.36	$P_2(5)$	$S_2(0)$	
03.664	3	371.71			
03.825	5	370.32	$P_2(5)$		
03.995	10	368.85		$R_2(2)$	
04.212	11	366.98		$R_2(2)$	$S_2(7)$
04.780	3	362.09	$O_2(3)$		
04.977	12	360.88	$P_2(6)$		
05.201	4	358.45	$P_2(6)$		
05.587	11	355.13		$R_2(1)$	
05.852	2	352.84		$R_2(1)$	
05.915	12	352.30			$S_2(6)$
06.304	2	348.94			
06.328	12	348.73	$P_2(7)$		

Table XI—(continued).

λ (I.A.).	i .	ν .	Classification.		
			${}^2\Pi_2 - {}^2\Sigma$.	${}^2\Pi_1 - {}^2\Sigma$.	${}^2\Pi_0 - {}^2\Sigma$.
2406.542	4	29346.89	$P_2(7)$		
07.320	5	340.19		$R_2(0)$	
07.692	8	336.99	$P_1(8)$		
07.810	11	335.97			$S_2(5)$
07.879	3	335.37	$P_2(8)$		
08.394	4	330.95	$O_1(4)$		
08.963	7	326.14			
09.065	8	325.18	$P_1(9)$		
09.238	3d	323.68	$P_2(9)$	$Q_1(1)$	
09.385	6	322.43		$Q_2(2)$	
09.451	8	321.83		$Q_1(2); Q_2(1)$	
09.712	0	319.61		$Q_2(2)$	
09.808	11	318.78		$Q_1(3); Q_2(3)$	
09.916	11	317.86			$S_2(4)$
10.070	2	316.53		$Q_2(3)$	
10.277	10d	314.75		$Q_1(4); Q_2(4)$	
10.479	7	313.01	$P_1(10)$		
10.541	7	312.48		$Q_2(4)$	
10.654	2	311.53	$P_2(10)$		
10.817	7	310.11		$Q_2(5)$	
10.899	7	309.67		$Q_1(5)$	
11.113	8	307.57		$Q_2(5)$	
11.462	5	304.57		$Q_2(6)$	
11.547	5	303.84		$Q_1(6)$	
11.770	7	301.92		$Q_2(6)$	
11.898	5	300.83	$O_1(5)$		
11.933	5	300.53	$P_1(11)$		
12.233	12d	297.95		$Q_2(7)$	$S_2(3)$
12.295	4	297.42		$Q_1(7)$	
12.513	11	295.54		$Q_2(7)$	
13.052	11	290.92		$Q_2(8)$	
13.141	3	290.16		$Q_1(8); P_1(2)$	
13.351	11	288.35		$Q_2(8); P_2(2)$	
13.478	4	287.27	$P_1(12)$		
13.630	0	285.96			
13.954	2	283.18		$Q_2(9)$	
14.093	2	281.99		$Q_1(9)$	
14.292	8	280.28		$Q_2(9)$	
14.768	0	276.20		$O_1(2)$	
14.794	11	275.98			$S_2(2)$
14.979	1	274.39		$Q_2(10)$	
15.104	4	273.32			
15.116	4	273.22		$Q_1(10)$	
15.274	4	271.87	$O_1(6)$		
15.314	13	271.52		$Q_2(10); P_1(3)$	
15.571	0	269.32		$P_2(3)$	
16.108	1	264.71		$Q_2(11)$	
16.291	1	263.15		$Q_1(11)$	
16.454	7	261.75		$Q_2(11)$	
16.807	3	258.72			
17.354	0	254.04		$Q_2(12)$	
17.587	0	253.23		$Q_1(12)$	
17.614	12	251.82			$S_2(1)$
17.682	12	251.24		$Q_2(12); P_1(4)$	
17.928	3	249.14		$P_2(4)$	
18.636	10	242.08	$O_1(7)$		
18.960	2	240.13		$Q_2(13); O_1(3)$	

Table XI—(continued).

λ (I.A.).	i .	ν .	Classification.		
			${}^1\Pi_2 - {}^1\Sigma$.	${}^1\Pi_1 - {}^1\Sigma$.	${}^1\Pi_0 - {}^1\Sigma$.
3419.063	4	29239.43			
19.571	11	235.08			$R_2(6)$
19.590	11	234.92			$R_2(7)$
19.708	11	233.90			$R_2(5)$
19.825	11	232.91			$R_2(8)$
19.893	3	232.33			$R_2(6); R_2(7)$
19.995	3	231.46			$R_2(5)$
20.070	9	230.81			$R_2(4)$
20.131	2	230.30		$P_1(5)$	$R_2(8)$
20.216	9	229.57			$R_2(9)$
20.360	9	228.33		$P_2(5)$	$R_2(4)$
20.553	3	226.69			$R_2(9)$
20.683	11d	225.60			$S_2(0); R_2(3)$
20.762	6	224.73			$R_2(10)$
20.943	9	223.36			$R_2(3)$
21.128	2	221.77			$R_2(10)$
21.486	1	218.72			
21.518	12	218.44			$R_2(2)$
21.778	11	216.23			$R_2(2)$
21.883	0	215.32			$R_2(11)$
21.950	6	214.76	$O_1(8)$		
22.154	2	213.02			
22.401	6	210.90			$R_2(12)$
22.659	12d	208.70		$P_1(6)$	$R_2(1)$
22.876	12d	206.86		$P_2(6)$	$R_2(1)$
23.181	2	204.25		$O_1(4)$	
23.444	5	202.01			$R_2(13)$
23.820	0	198.80			$R_2(13)$
23.916	1	197.98			
24.440	0	193.51			
24.648	5	191.74			$R_2(14)$
24.823	1	190.24			
24.995	0	188.79			$R_2(14)$
25.258	9	186.54	$O_1(9)$		
25.304	9	186.15		$P_1(7)$	
25.531	7	184.30		$P_2(7)$	
25.816	0	181.79			
26.005	2	180.18			$R_2(15)$
26.499	5	175.97			
26.543	2	175.60			$Q_2(2)$
26.822	10	173.22			$Q_2(2)$
27.165	0	170.30			
27.422	8	168.11			$Q_2(3); Q_2(3)$
27.504	4	167.42		$O_1(5)$	$R_2(16)$
27.690	11	165.84			$Q_2(3)$
27.853	0	164.45			
28.023	7	163.01		$P_1(8)$	
28.217	6	161.35		$P_2(8)$	
28.581	12d	158.42	$O_1(10)$		$Q_2(4); Q_2(4)$
28.694	12d	156.19			$Q_2(4)$
29.223	1	152.80			$R_2(17)$
29.902	12	147.02			$Q_2(5)$
29.936	0	146.74			$Q_2(5)$
30.196	12	144.53			$Q_2(5)$
30.823	6	139.20		$P_1(9)$	
31.010	6	137.61		$P_2(9)$	
31.065	0	136.89			$R_2(18)$

Table XI—(continued).

λ (I.A.).	i .	ν .	Classification.		
			$^3\Pi_2 - ^3\Sigma$.	$^3\Pi_1 - ^3\Sigma$.	$^3\Pi_0 - ^3\Sigma$.
3431.491	12	29133.53			$Q_2(6)$
31.569	0	132.87			$Q_1(6)$
31.798	12	130.92			$Q_2(6)$
31.909	8	129.98	$O_1(11)$	$O_1(6)$	
32.477	2	125.16			$P_1(3)$
32.756	2	122.79			$P_2(3)$
33.281	11	118.35			$Q_2(7)$
33.382	0	117.49			$Q_1(7)$
33.597	11	115.67			$Q_2(7)$
33.688	3	114.90		$P_1(10)$	
33.880	5	113.25		$P_2(10)$	
35.263	12	101.55	$O_1(12)$		$Q_2(8)$
35.358	2	100.74			$Q_1(8); P_1(4)$
35.586	11	998.81			$Q_2(8); P_2(4)$
36.428	4	991.68		$O_1(7)$	
36.670	3	989.62		$P_1(11)$	
36.838	4	988.21		$P_2(11)$	
37.389	0	983.55			
37.412	8	983.35			$Q_2(9)$
37.569	0	982.02			$Q_1(9)$
37.757	8	980.43			$Q_2(9)$
38.491	2	974.23			$P_1(5)$
38.728	8	972.22	$O_1(13)$		$P_2(5)$
39.715	0	963.88		$P_1(12)$	
39.738	9	963.68			$Q_2(10)$
39.889	3	962.41		$P_2(12)$	$Q_1(10)$
40.084	5	960.76			$Q_2(10)$
41.026	4	952.80		$O_1(8)$	
41.862	2	945.75			$P_1(6)$
42.089	4	943.84	$O_1(14)$		$P_2(6)$
42.222	8	942.71			$Q_2(11)$
42.575	3	939.73			$Q_1(11)$
42.887	1	937.10		$P_1(13)$	
43.043	4	935.79		$P_2(13)$	
44.852	6	920.54			$Q_2(12)$
45.195	3	917.65			$Q_1(12)$
45.455	2	915.46			$P_1(7)$
45.681	9d	913.56	$O_1(15)$	$O_1(9)$	$P_2(7); O_1(5)$
46.114	2	909.91			
46.147	1	909.64		$P_1(14)$	
46.285	3	908.46		$P_2(14)$	
47.626	6	28997.19			$Q_2(13)$
48.003	1	994.01			$Q_1(13)$
49.261	1	983.44			$P_1(8)$
49.465	4	981.73			$P_2(8)$
49.531	1	981.17		$P_1(15)$	
49.657	2	980.11		$P_2(15)$	
50.477	3	973.23		$O_1(10)$	$O_1(6)$
50.548	3	972.64			$Q_2(14)$
50.933	1	969.41			$Q_1(14)$
53.028	0	951.83		$P_1(16)$	
53.151	1	950.79		$P_2(16)$	
53.251	0	949.95			$P_1(9)$
53.349	0	949.13			
53.443	5	948.34			$P_2(9)$
53.624	3	946.83			$Q_2(15)$
54.019	1	943.52			$Q_1(15)$

Table XI--(continued).

λ (I.A.).	i .	ν .	Classification.		
			$^3\Pi_2 - ^3\Sigma$.	$^3\Pi_1 - ^3\Sigma$.	$^3\Pi_0 - ^3\Sigma$.
3455.330	3	28932.53		$O_1(11)$	
55.791	0	928.68			$O_1(7)$
56.750	0	920.65			
56.835	1	919.94			$Q_2(16)$
57.245	2	916.51			$Q_2(16)$
57.422	0	915.03			$P_2(10)$
57.605	4	913.50			$P_2(10)$
60.215	1	891.69			$Q_2(17)$
60.258	1	891.33		$O_1(12)$	
60.489	0	889.42			
60.599	0	888.48			$Q_2(17)$
61.283	0	882.78			
61.400	0	881.80			$O_1(8)$
61.924	3	877.43			$P_2(11)$
63.737	0	862.31			$Q_2(18)$
64.363	0	857.10			
65.299	0	849.30		$O_1(13)$	
65.449	0	848.05			
66.403	2	840.12			$P_2(12)$
67.216	-1	833.35			$O_1(9)$
67.413	1	831.72			$Q_2(19)$
68.403	0	823.48			
69.785	0	812.00			
70.422	0	806.72		$O_1(14)$	
71.028	1	801.69			$P_2(13)$
71.282	0	799.57			$Q_2(20)$
72.567	-1	788.92			
73.189	-1	783.76			$O_1(10)$
74.234	-1	775.11			
75.333	-1	766.01			$Q_2(21)$
75.656	-1	763.33		$O_1(15)$	
75.772	-1	762.38			$P_2(14)$
77.984	0	744.08			
78.198	-1	742.31			
83.757	-1	696.45			
85.709	0	680.39			

Summary.

(1) The λ 3400 band attributed by Geuter to a hydride of phosphorus has been photographed in the second order of the 10-foot grating. Measurements of the wave-lengths have been made with reference to the iron standards recommended by the International Astronomical Union in 1928.

(2) The band has been completely analysed into 27 branches, and is believed to afford the most complete data at present available for a $^3\Pi \rightarrow ^3\Sigma$ transition.

(3) The fine structure arising from the $^3\Sigma$ level has been resolved and the observed separations compared with Kramers' theoretical formula. Good agreement is obtained.

(4) The $^3\Pi$ levels are found to be inverted. An approximate estimation of the electronic energy separations between the three component levels shows that they are not equally spaced but that $^3\Pi_2 - ^3\Pi_1 = -121 \text{ cm.}^{-1}$, while $^3\Pi_1 - ^3\Pi_0 = -111 \text{ cm.}^{-1}$.

(5) A complete catalogue of wave-lengths with estimated intensities and classification is appended.

In conclusion, the author wishes to express his deep gratitude to Prof. A. Fowler for his continued interest and encouragement during the course of this work.

DESCRIPTION OF PLATE 19.

The Plate shows an enlargement of the photograph of the $\lambda 3400$ band of PH taken in the second order of the 10-foot grating. The arrangement of the lines into branches is marked below each portion of the spectrum. The branches are divided into three sections (a), (b) and (c), according as they belong to the transitions $^3\Pi_0 \rightarrow ^3\Sigma$, $^3\Pi_1 \rightarrow ^3\Sigma$ and $^3\Pi_2 \rightarrow ^3\Sigma$ respectively.

The Absorption Spectrum of Lithium Vapour.

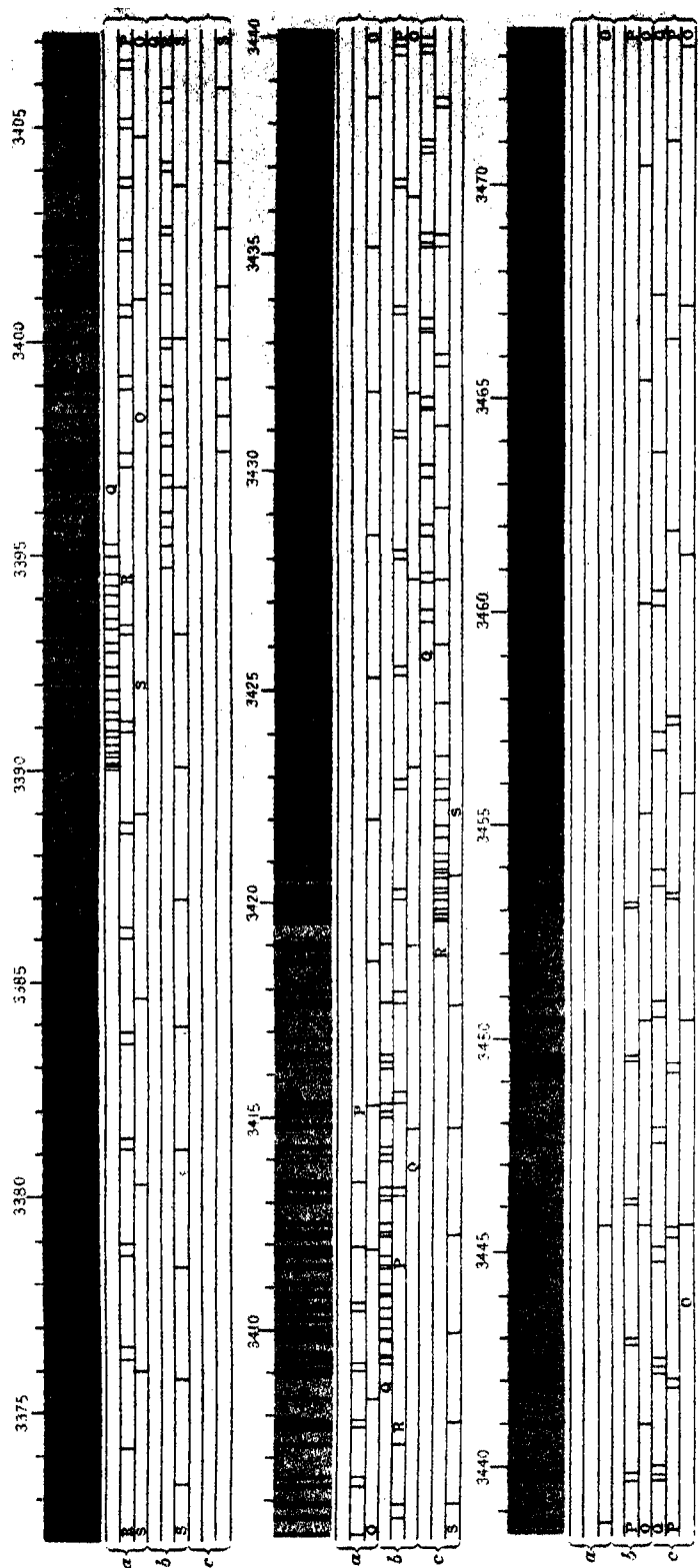
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The absorption spectrum of lithium vapour has been previously studied under low dispersion by several workers. There are two main features of interest in it, the principal series, extending from the first line in the red at 6708 Å. to a limit at 2299 Å., and the band structures in the blue-green, 4500–5500 Å. and in the red, 6800–7700 Å. The observation of the spectrum is attended by two principal difficulties: first, lithium has a high boiling point, in the neighbourhood of 1400° C. at normal pressure, and it is strongly corrosive at high temperatures; secondly, the limit of the series has a very low wave-length, this fact rendering it very difficult to use a source not peculiarly rich in ultra-violet light for the transmission of continuous radiation through the vapour.

Bevan, the first worker to publish any data* relating to this spectrum, heated

* 'Proc. Roy. Soc.,' A, vol. 83, p. 43 (1910); A, vol. 85, p. 54 (1911); A, vol. 86, p. 330 (1911–12).



lithium in a double-walled steel tube and used as illuminant a condensed cadmium spark; he used a quartz spectrograph and measured the wave-lengths of the first 41 members of the principal series with estimated error $0.2-0.3 \text{ \AA}$., deriving a Hicks' formula for their wave-numbers.

Zeeman has observed the line at $6708 \text{ \AA}$. as a close doublet* in absorption, having a separation $0.144 \text{ \AA}$. This separation is small in comparison with the value, $0.6 \text{ \AA}$., which would be expected from the fact that the corresponding doublet separations for the other alkali metals are roughly proportional to the squares of the atomic weights.

Trumphy conducted photometric measurements† on the lines of the principal series in absorption; he measured the absorption coefficients at the middle of each line and also the half-breadths of the lines. Hence he obtained results which confirmed the predictions of Holtzmark's theory of the broadening of the lines.

The band structures in the visible region were the subject of rough measurements by Naraiyan and Gunnaiya,‡ and they have recently been analysed in detail by K. Wurm,§ and A. Harvey and F. A. Jenkins.||

One of the prime objects of the writer's work was to obtain more accurate values for the wave-lengths of the principal series. By photographing them on a Rowland grating spectrograph giving in the first order a dispersion of $4.3 \text{ \AA}$. per millimetre and a theoretical resolving power 6.4×10^4 the estimated errors have been reduced to values in the neighbourhood of $0.01 \text{ \AA}$.

The absorption apparatus consisted of two steel tubes, one being 150 cm . long and $1\frac{1}{2}$ inches diameter and the other 115 cm . long, situated centrally in the former, inside which it just fitted; the ends of the former tube were ground off truly and closed by a quartz plate and quartz lens respectively so that a parallel beam of light could be thrown down the tube from a source at the principal focus of the lens. This beam, after passing through the quartz plate, was brought to a focus just in front of the slit of the spectrograph by a second quartz lens. The lithium metal was placed in small pieces inside the inner steel tube between two suitably shaped pieces of steel which acted as barriers to the lithium when molten. The lithium was not specially purified, except by washing in benzene to dissolve the hydrocarbon oil in which it had

* 'Proc. Amst. Acad.', vols. 15-16 (1914).

† 'Z. Physik,' vol. 44, p. 575 (1927).

‡ 'Proc. Roy. Soc., A,' vol. 106, p. 51 (1924).

§ 'Z. Physik,' vol. 58, p. 562 (1929); vol. 59, p. 35 (1929).

|| 'Phys. Rev.,' vol. 35, p. 132, Abstracts (1930); 'Phys. Rev.,' vol. 34, p. 1266 (1929).

been kept and scraping off subsequently the black coating of what was probably mainly oxide. The outer tube was also provided with a side tube near each end for the exhaustion of contained air and the admission of hydrogen respectively; the latter was purified by passage through water and silver nitrate solution, and dried by passage through strong sulphuric acid.

The heating of the tube was provided by two nichrome wire coils, 16 S.W.G., in parallel, wound on an asbestos sheet wrapped round the outer steel tube, this winding being then lagged with five layers of asbestos cord; the length of tube wound with the coils was about 90 cm. In the case of each coil 10 cm. of this length at each end were wound with a spacing between adjacent turns of $\frac{1}{8}$ cm., the 70 cm. between being wound with spacing 1 cm. This spacing of the winding gave a very uniform temperature distribution along the length of the tube and moreover was found absolutely necessary in order to prevent a rapid distillation of the lithium from the heated parts of the tube. A further precaution to prevent this rapid distillation of the lithium was taken by passing in hydrogen as mentioned above. It was found, however, that any hydrogen passing in was absorbed by the lithium or diffused out through the red-hot walls of the tube, so that the pressure in the tube was always too small to be observed with a pressure gauge of simple type.

An estimate of the temperature of the lithium vapour was obtained by means of a thermocouple situated at the middle of the heating coil. This enabled the conditions to be reproduced consistently. It was found that the principal series was best reproduced when the temperature indicated by the thermocouple was between 870° – 930° C. Above the latter temperature the lines broadened considerably, even the higher members broadening to an extent rendering impossible the accurate measurement of their wave-lengths; in addition, they appeared not to contrast so well with the continuous background.

Considerable difficulty was experienced in the attempt to obtain a photograph of the principal series by reason of the very short wave-length of the series limit. A carbon arc was used as the source of continuous radiation and the strength of this continuous radiation of wave-length in the neighbourhood of the limit was so small that the fogging effect on the photographic plate of stray white light scattered from the grating was comparable with it and thus the comparatively faint absorption lines near the limit were not observable. The use of a cadmium spark, following Bevan's usage, was not found practicable because of the difficulty of putting enough energy into it to permit of a reasonable exposure time. After various expedients had been tried to overcome the difficulty without success, it was finally found that considerable improvement

could be made by cleaning the ruled surface of the grating. This was accomplished by coating the surface with a solution of guncotton in amyl acetate, allowing this to dry thoroughly, and then stripping off the resultant very thin film as in Wallace's method of constructing replicas of plane gratings* ; three of these films were applied in succession. It was found that, although the strength of the radiation diffracted from the grating was not very much increased, the amount of stray white light scattered from it was very much diminished and the absorption lines became plainly observable.

Finally, three photographs of the region 2250–3400 Å., which included the principal series from the second member to the series limit, were taken, using Hilger H.S. carbons as a source of continuous radiation. The spectrum of the Pfund iron arc, burning under the standard conditions specified by the International Astronomical Union,† was used as comparison spectrum. In each case the temperature indicated by the thermocouple was 900° C. and the pressure in the absorption tube too low to measure by a pressure gauge of simple type. On each of these plates the wave-lengths of the lines of the principal series were measured for two settings of the plate on the comparator table ; two settings were used in order to minimise the error due to the fact that the screw of the comparator showed a periodic error which was sufficient to produce an appreciable effect on the measurements. The means of these were taken as the most probable values for the wave-lengths, and the estimated errors were obtained by a study of their differences.

The wave-lengths of the iron arc spectrum given in Kayser's "Handbuch der Spectroscopie," vol. 7, were used as standards of comparison, but in the neighbourhood of the series limit there are not enough lines of sufficient accuracy ; the only recorded lines in this region are those of Schumacher, which are given only to 0.01 Å. This deficiency of accurately measured lines was made up in the following way. From a list of energy levels and corresponding term values for the iron arc spectrum, given by Meggers,‡ which had been derived from lines of longer wave-length, the wave-lengths of a number of possible lines in the neighbourhood of the limit were deduced ; the existence of these was confirmed by comparison with the list of approximate wave-lengths given by Schumacher and they were then used as standards ; the error in such values was probably 0.002–0.003 Å. The need for further work in

* 'Astrophys. J.,' vol. 22, p. 123 (1905).

† Baly, "Spectroscopy," vol. 2, or 'Int. Astron. Union Trans.,' vol. 1, p. 36 (1922).

‡ 'Astrophys. J.,' vol. 60, p. 60 (1924).

setting up standards of wave-length on the short wave-length side of 2800 Å. in the iron arc spectrum is thus indicated.

A table of data relating to the principal series is appended (Table I). In the first column is given the number of the line; that in the red at 6708 Å. is counted as $m = 1$ and thence upwards to the series limit.* In the second and third columns are given the observed wave-lengths and corresponding wave-numbers *in vacuo* (obtained from Kayser's "Tabellen der Schwingungszahlen"). In the fourth column headed (O — C) are given the differences between the observed wave-numbers and those calculated from a Hicks' formula

$$n = 43486 \cdot 87 - \frac{109679 \cdot 2}{\left\{ m + 0 \cdot 950570 + \frac{0 \cdot 008643}{m} \right\}^2}$$

This was derived from the observed values of the wave-numbers for the lines 2, 3, 4.

In the fifth and sixth columns the estimated errors in wave-number and wave-length are given respectively, and in the last column Bevan's results for the wave-lengths are to be found. It will be seen that there is a considerable improvement on Bevan's accuracy.

A value for the wave-number of the series limit has been derived from the Hicks' formula. Taking into account the (O — C) values, the best value for the limit of the series appears to be $43486 \cdot 76 \pm 0 \cdot 28$ cm. corresponding to a wave-length $2298 \cdot 837 \pm 0 \cdot 015$ Å.

The wave-length of the first line at 6708 Å. was not measured by the writer; the value given is that obtained by Fabry and Perot.†

It was found that the absorption line $m = 10$, wave-length approximately 2348·4 Å. according to Bevan, could not be detected on any of the plates used for measurement. This is probably due to the fact that it has a wave-length intermediate between those of two iron lines very close together—2348·18 Å. and 2348·32 Å.—so that light from these two lines (due to the small quantities of iron present as impurities in the carbon arc) would obliterate this rather faint absorption line.

Mention must be made of a peculiar spectrum which was observed at temperatures higher than about 950° C., in the neighbourhood of the second member of the principal series at 3233 Å.; this is probably analogous to that observed

* The numbering of the terms is that adopted by Bevan and followed by Fowler in his "Report on series in Line Spectra," and differs from that adopted in the tables of Paschen-Götze; the last-named number λ 6708 $m = 2$, λ 3233 $m = 3$, and so on.

† 'C. R.,' vol. 130, p. 492 (1900).

Table I.—List of Data relating to the Principal Series of Lithium.

m.	Wave-length in Å.U.	Wave-number cm. ⁻¹ .	(O - C) cm. ⁻¹ .	Estimated errors.		Bever's wave-lengths.
				$\delta\alpha$.	$\delta\lambda$.	
1	6707.844	14903.81	-9.73	—	—	6708.0
2	3232.660	30925.38	—	0.10	0.01	3232.66
3	2741.204	36469.55	—	0.20	0.015	2741.29
4	2562.312	39015.56	—	0.23	0.015	2562.52
5	2475.061	40390.84	-0.36	0.24	0.015	2475.05
6	2425.426	41217.35	-0.16	0.14	0.008	2425.47
7	2394.386	41751.63	-0.67	0.35	0.020	2394.46
8	2373.541	42118.27	+0.13	0.32	0.018	2373.8
9	2358.928	42379.16	-0.21	0.36	0.020	2359.3
10	(2348.221)	(42572.37)	—	—	—	2348.4
11	2340.153	42719.14	-0.13	0.36	0.020	2340.4
12	2333.986	42832.92	-0.07	0.25	0.015	2334.2
13	2329.016	42923.39	+0.03	0.25	0.015	2328.9
14	2325.109	42995.51	-0.71	0.15	0.008	2325.1
15	2321.878	43055.34	-0.47	0.28	0.015	2321.8
16	2319.180	43105.42	+0.26	0.37	0.020	2319.2
17	2316.947	43146.96	+0.45	0.15	0.008	2317.0
18	2315.075	43181.84	+0.37	0.28	0.015	2315.1
19	2313.491	43211.39	+0.09	0.15	0.008	2313.5
20	2312.113	43237.16	+0.16	0.56	0.030	2312.2
21	2310.938	43259.14	-0.11	0.37	0.020	2311.0
22	2309.880	43278.96	+0.31	0.28	0.015	2309.9
23	2308.969	43296.03	+0.36	0.19	0.010	2308.9
24	2308.147	43311.45	+0.76	0.38	0.020	2308.2
25	2307.435	43324.81	+0.81	0.28	0.015	2307.4
26	2306.818	43336.40	+0.53	0.28	0.015	2306.82
27	2306.286	43346.39	-0.09	0.19	0.010	2306.40
28	2305.833	43354.91	-1.09	0.19	0.010	2305.82
29	2305.365	43363.71	-0.89	0.28	0.015	2305.36
30	2304.921	43372.06	-0.32	0.29	0.015	2304.94
31	2304.589	43378.31	-1.12	0.38	0.020	2304.58

in the neighbourhood of the second member of the principal series of sodium by R. W. Wood. It was of a complicated many-lined structure most pronounced in the immediate vicinity of λ 3233 and extending about 200 Å. on either side. No sort of order or band head was discernible in this structure.

In addition to the series absorption lines, a few other absorption lines were found on the plates. Two lines belonging to a series ($1s - md$) not in accordance with the selection principle were observed:—

(i) ($1s - 3d$) which has been observed before by Sowerby and Barratt* under similar conditions not only in the case of lithium but also in the case of the other alkali metals. In this case it was fairly strongly pronounced and its wave-length was measured as 3195.716 Å.

* 'Proc. Roy. Soc.,' A, vol. 110, p. 190 (1926).

(ii) ($1s - 4d$) which has been observed before by Sowerby and Barratt only in the case of caesium; this was very faint and had a wave-length $2729\cdot706$ A. A faint absorption line was also observed at $2852\cdot18$ A.; this is probably due to the presence of magnesium as an impurity.

The writer would like to take this opportunity of expressing his thanks to Prof. S. R. Milner for his advice and encouragement during the course of this work.

APPENDIX.

List of Standard Wave-lengths in the Iron Arc Spectrum derived from Term Values given in Meggers' Paper.

The nomenclature of the term values— A_4, S_6 , etc.—are those used in Meggers' paper. The wave-lengths found under the heading "Schumacher" are the values obtained by Schumacher and listed in Kayser's "Handbuch."

Combination.	Wave-length derived from term values.	Schumacher.
$(A_4 - S_6)$	2329·642	2329·60
$(A_4 - S_6)$	2298·165	2298·18
$(A_4 - S_6)$	2276·011	2275·98
$(A_4 - S_6)$	2320·354	2320·33
$(A_4 - S_6)$	2297·783	2297·78
$(A_4 - S_6)$	2284·118	2284·06
$(A_4 - S_6)$	2313·104	2313·07
$(A_4 - S_6)$	2299·216	2299·22
$(A_4 - S_6)$	2293·845	
$(A_4 - S_6)$	2308·955	2308·99
$(A_4 - S_6)$	2303·579	2303·56
$(A_4 - S_6)$	2308·364	

The Passage of an Electron Beam through a Field-Free Enclosure.

By F. L. ARNOT, Ph.D., Trinity College, Cambridge, Isaac Newton Student.

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PART I.

Introduction.

A method which is frequently employed in investigating collision problems consists essentially of firing a directed beam of electrons into a collision chamber containing the gas to be investigated at a pressure of a few hundredths or thousandths of a millimetre. The collision chamber generally contains a system of "grids" between which various potentials can be put, so as to draw out of the path of the beam the products of collision which are then received on an electrode or Faraday cylinder placed behind the last grid. When these grids are all at the same potential the collision chamber is generally supposed to be field-free, and the ions formed by electron impact might be supposed to have energies determined by the temperature of the gas in the chamber.

In particular, an apparatus employing an electron beam in a "field-free" enclosure has been used by a number of investigators to examine the angular scattering of electrons in gases. These experiments have considerable interest, and in view of the large amount of work that is being done in this comparatively new field of investigation it is of importance to determine to what extent an enclosed space around an electron beam is truly field-free; for it will be clearly seen that the existence of a potential gradient inside the collision chamber will, if sufficiently great, seriously alter the shape of the angular scattering curve.

The present paper describes an experimental investigation of the fields set up by the passage of an electron beam through an enclosure having equipotential boundaries. The method employed was to examine the angular and velocity distributions of the positive ions formed along the path of the electron beam. If the inside of the collision chamber were truly field-free the positive ions would diffuse out equally in all directions with their velocities of thermal agitation. Owing to the large difference in mass between the ion and the electron, the energy that the positive ion receives on formation by its collision

with an electron is negligible compared to its thermal energy. Calculation shows that the maximum amount of energy that a mercury atom can receive by collision with an electron of 100 volts energy is 2.5×10^{-4} volt, whereas the thermal energy of the atom at room temperature (20°C.) is 3.8×10^{-2} volt.

Apparatus.

The first experiments were made with the same apparatus as the author employed to determine the angular scattering of electrons in mercury vapour.* The reader is referred to this paper for a full description of the apparatus. It will be sufficient to say here that the apparatus consisted essentially of a large glass bulb through which passed a sharp electron beam having a diameter of cross section of about 1 millimetre. A Faraday cylinder having two collimating slits in the shield enclosing it could be rotated around inside the bulb so as to receive electrons scattered at any angle to the direction of the electron beam. The bulb was coated on the inside with magnesium, and this was connected to the shield around the Faraday cylinder and to the anode of the electron gun. The inside of the bulb was consequently bounded on all sides by an equipotential surface. The gas employed was mercury vapour at a pressure of about 0.001 mm., and the velocity of the primary electron beam was about 80 volts.

It was noticed during the electron-scattering experiments that at angles near 90° a strong positive current was superimposed upon the negative current due to the electrons scattered at these angles. This positive current was completely stopped by a retarding potential of 2 or 3 volts, showing that the effect was not due to a photo-electric emission of electrons from the Faraday cylinder. In order to study this effect the potential between the Faraday cylinder and its outer shield was kept about 20 to 40 volts greater than the potential applied to the primary electron beam. This prevented any electrons from entering the Faraday cylinder.

By measuring the positive ion current at intervals of 5° from -180° to $+180^\circ$ the angular distribution of the positive ions was determined. A typical curve is shown in fig. 1 in which the ordinates represent the magnitude of the positive ion current received by the Faraday cylinder in arbitrary units.

In order to investigate the angular and velocity distribution of the positive ions in more detail an improved form of apparatus was designed and built. This is shown in fig. 2. The electron gun consisted of the tungsten filament F,

* Arnot, 'Proc. Roy. Soc.,' A, vol. 125, p. 660 (1929).

entirely enclosed within the long nickel cylinder, C_1 , containing two holes S_1 and S_2 , each of 1 mm. in diameter. The filament leads ran closely parallel

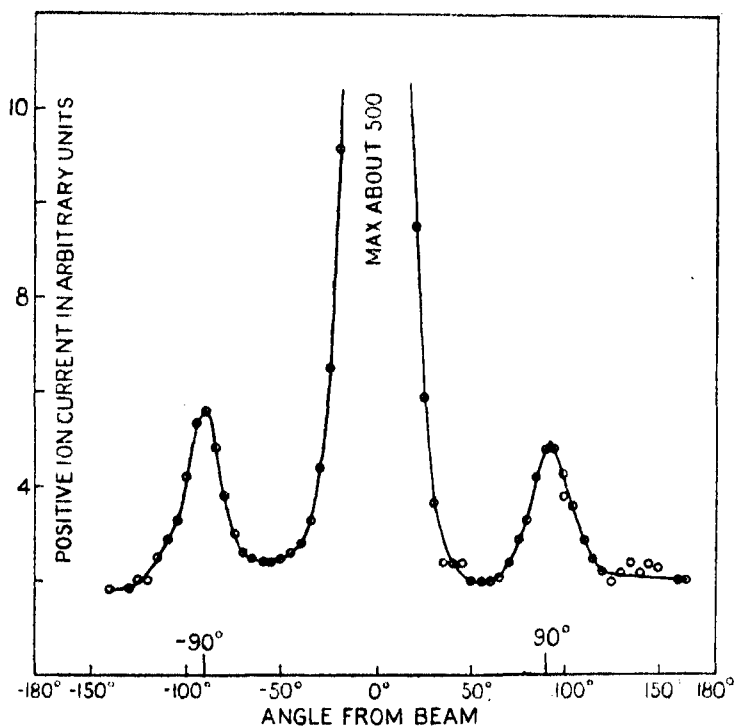


FIG. 1.—Angular Distribution of Positive Ions.

to each other so as to make the magnetic field in the collision chamber due to the filament current as small as possible. Inside the collision chamber the leads were enclosed in nickel tubing so as to shield the chamber from the electric field due to the potential of the filament leads. The gun could be rotated about the axis O through nearly 360° by means of the small ground glass joint G_1 , while the large joint, G_2 , enabled the entire gun to be removed for adjustment and filament renewal. When running in mercury vapour the electron beam could be clearly seen. It was quite sharp throughout its whole length, showing practically no tendency to diverge, its diameter of cross section being about 1 millimetre.

The receiving system consisted of the three concentric cylinders C_2 , C_3 , C_4 containing the slits S_3 , S_4 , S_5 and the concentric Faraday cylinder, K . The dimensions of these slits were respectively 8 mm. $\times$ 0.2 mm., 5 mm. $\times$ 0.2 mm., 2 mm. $\times$ 2 mm., and the three slits were equally spaced

5 mm. apart. The two cylinders C_2 and C_3 were insulated from each other by glass beads, B, and were carried by the ground glass joint G_3 . The Faraday

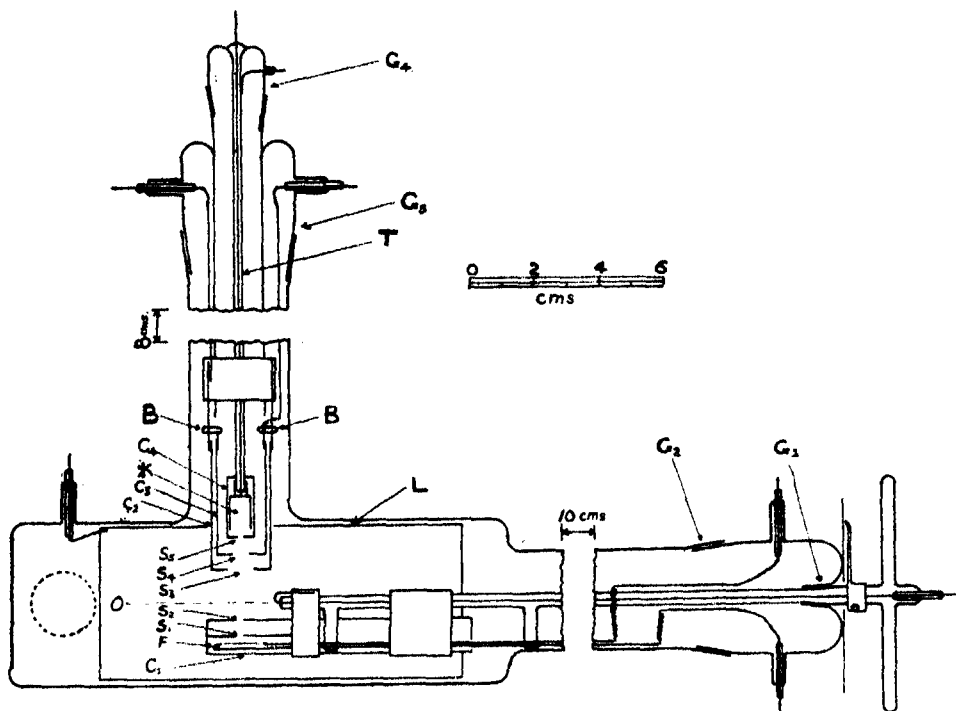


FIG. 2.—Apparatus.

cylinder K, which was completely enclosed in the shielding cylinder C_4 , was carried on the quartz tube T and the small quartz ground joint G_4 . The tube, T, containing the lead to the Faraday cylinder was enclosed within a closely fitting nickel cylinder for the purpose of electrostatic shielding. The entire receiving system could be taken out for adjustment by means of the ground glass joint G_3 .

The slits S_1 , S_2 , S_3 , S_4 could be easily lined up when the Faraday cylinder and shield were removed by viewing the filament, which was heated to a dull red, through the open joint G_4 . The inside of the collision chamber was lined with the large nickel cylinder L. All metal parts, including leads, consisted of out-gassed nickel. The glass work was of pyrex, and the whole apparatus up to within a few centimetres of the joints was baked out at a temperature of 500°C . before each run. No difficulty was experienced in keeping the temperature of the grease joints below room temperature by means of water coolers during the baking out process.

The apparatus was connected through a mercury vapour trap to the usual pumping system, and a good "sticking vacuum" was obtained on a sensitive McLeod gauge. Tests with liquid air on the mercury vapour trap showed the presence of a single sharp electron beam at 0° . At all other angles no drift was observed showing that no appreciable amount of the primary electron beam was scattered from the slits S_1 , S_2 or from the lining L of the collision chamber. In these tests a small retarding potential of about 20 volts was applied between S_4 and S_5 , as large numbers of secondary electrons having energies of a few volts are obtained without this precaution. A wiring diagram is shown in fig. 3.

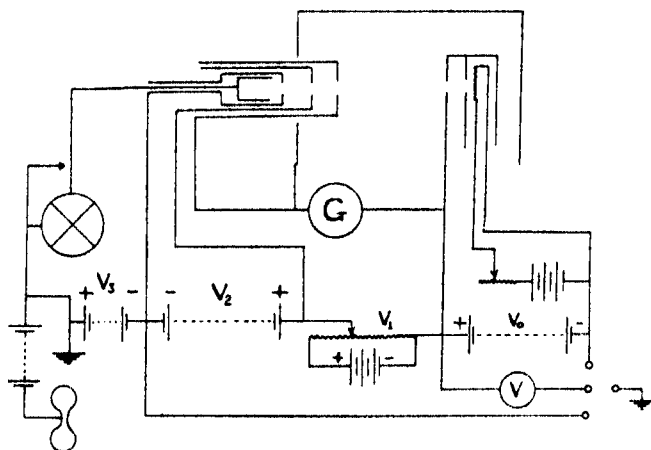


FIG. 3.—Wiring Diagram.

In describing the results obtained with this apparatus, the following symbols for the various potentials will be used :—

V_0 = potential between filament and gun slits, S_1 , S_2 .

V_1 = potential between S_3 and S_4 .

V_2 = potential between S_4 and S_5 .

V_3 = potential between S_5 and K. (K is earthed.)

The following conventional signs will be used :—

A potential which *repels* electrons is negative.

A potential which *repels* positive ions is positive.

The potential V_2 is always opposite to, and greater than V_0 , thereby preventing any electrons from reaching the Faraday cylinder. V_3 is employed to prevent the emission of secondary electrons from the Faraday cylinder, set free by the

impact of positive ions or by a photo-electric effect. V_1 , which is used in determining the velocity distribution of the positive ions, is applied by means of a post office box and two or three cells. The following results were all obtained in mercury vapour at room temperature.

Results.

(1) *The Angular Distribution of the Positive Ion.*— $V_0 = +109$ volts. $V_1 = \text{zero}$. $V_2 = -167$ volts. $V_3 = +83$ volts.

With the above arrangement of potentials the positive ion current to the Faraday cylinder was measured for different angular settings of the electron gun. When the electron beam is firing straight through the slits, S_3 , S_4 , the angle is zero. The angular distribution obtained is shown in fig. 4. It will be seen by comparing figs. 1 and 4 that the curve obtained is identical with the type of curve found with the old apparatus. In fig. 4 the readings obtained

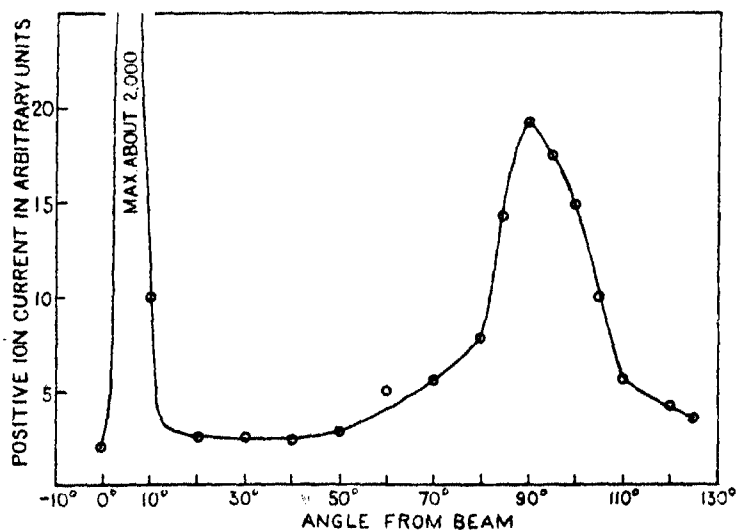


FIG. 4.—Angular Distribution of Positive Ions.

on one side only of the electron beam are shown. The same result was obtained at negative angles, *i.e.*, by taking readings on the other side of the electron beam.

It will be seen from figs. 1 and 4 that there are two peaks, one at 0° and one at 90° to the electron beam on both sides of it. The strong peak at 0° is due to the intense ionisation produced between the slits S_4 and S_5 by the primary electron beam, which at 0° is firing straight through these slits. The positive

ions so produced are then immediately accelerated into the Faraday cylinder by the field between the slits S_4 and S_5 which stops the electrons. The peak at 90° to the electron beam on both sides of it shows that the positive ions in the collision chamber are moving in directions at right angles to the electron beam.

(2) *Variation in Intensity of Peak at 90° with Electron Beam Current.*— $V_0 = +122$ volts. $V_1 = \text{zero}$. $V_2 = -163$ volts. $V_3 = +83$ volts.

With the above arrangement of potentials, readings of the positive ion current at 90° to the electron beam were taken for different values of the current in the electron beam. The value of the electron beam current, which was varied by altering the filament emission, was read off directly from the galvanometer, G , shown in fig. 3. In fig. 5, the intensity of the positive ion

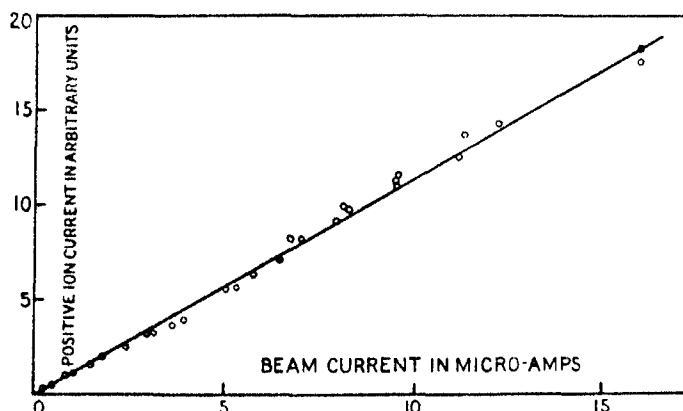


FIG. 5.—Relation between Positive Ion Current and Electron Beam Current.

current at right angles to the beam is plotted in arbitrary units against the current in the electron beam in micro-amperes. It will be seen from the figure that the positive ion current is a linear function of the density of ionisation along the path of the electron beam.

(3) *The Velocity Distribution of the Positive Ions.*—By setting the electron gun at 90° and applying retarding potentials between the slits S_3 and S_4 the velocity distribution of the positive ions was obtained. It was found that the mean velocity of the positive ions was a function of the velocity of the electrons in the beam. In fig. 6 are shown seven velocity distribution curves for different velocities, V_0 , of the electron beam. For each value of V_0 the positive ion current to the Faraday cylinder is plotted in arbitrary units against the retarding potentials in volts. For the sake of clearness in the figure some curves have been slightly displaced in a vertical direction. They are all drawn to the

same scale and the base line is drawn at the foot of those curves which have been displaced.

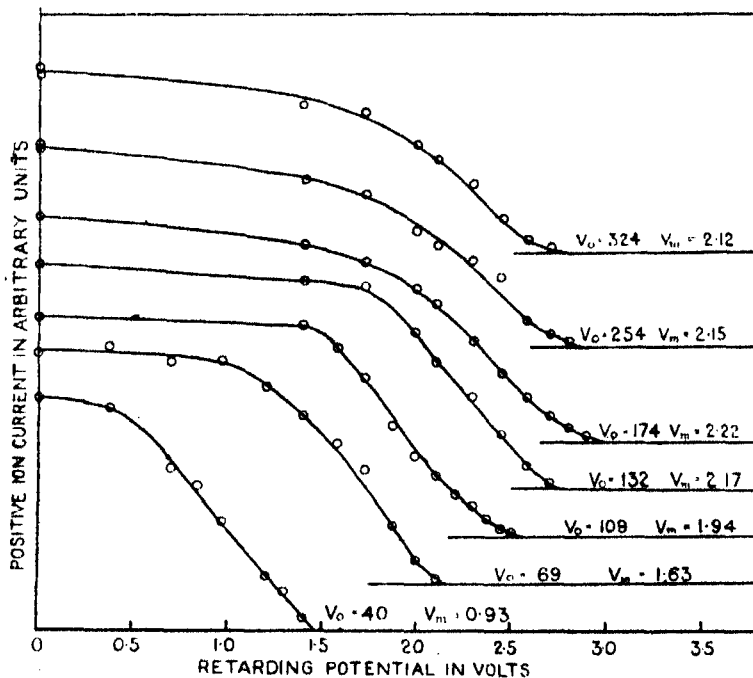


FIG. 6.—Velocity Distribution of Positive Ions.

It will be seen from the shape of the curves that the velocities of the positive ions are not strictly homogeneous but instead have a probability distribution, about a mean value. The mean velocity, V_m , of the ions is found in each case by taking the abscissa corresponding to the point where the positive ion current has fallen to half its full value. The values of the electron beam velocity V_0 , and the corresponding mean velocity of the positive ions, V_m , are marked on each curve.

(4) *Relation between Velocity of Ions and Velocity of Electrons.*—In fig. 7 the mean velocities of the positive ions are plotted as ordinates against the velocities of the electron beam. It will be seen that the positive ions have a maximum velocity of about 2.2 volts when the velocity of the electron beam is about 175 volts. The current in the electron beam was kept constant throughout this run at 20 microamps. for all values of V_0 . The striking similarity of this curve to Compton and Van Voorhis's curve for the efficiency of ionisation by electron impact as a function of the velocity of the electrons*

* Compton and Van Voorhis, 'Phys. Rev.', vol. 27, p. 729 (1926).

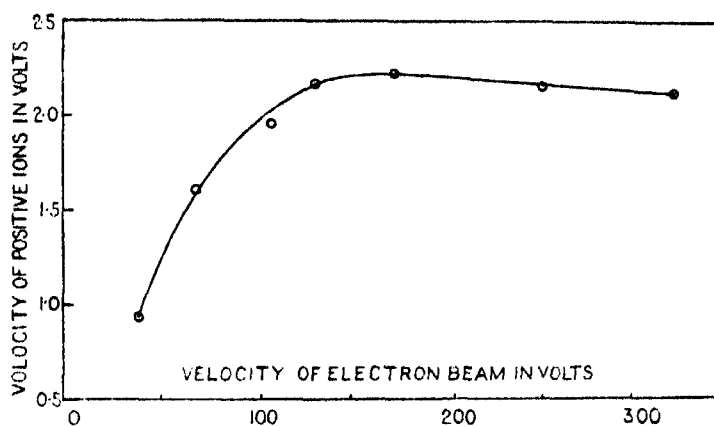


FIG. 7.—Relation between Velocity of Positive Ions and Velocity of Electron Beam.

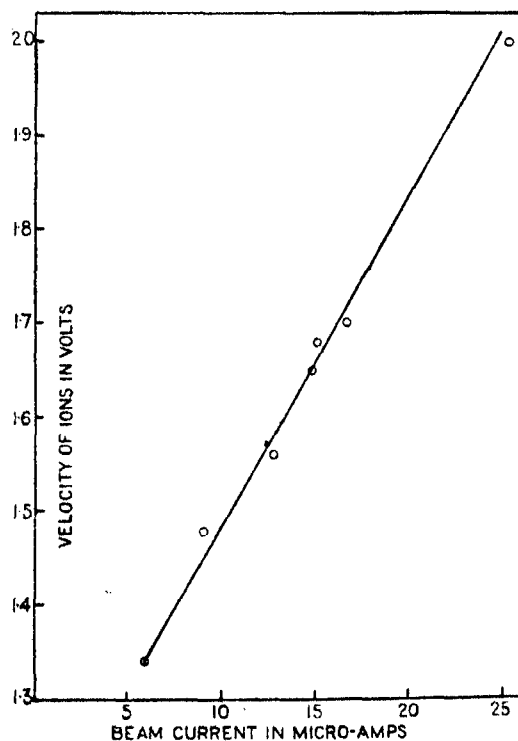


FIG. 8.—Relation between Velocity of Positive Ions and Electron Beam Current.

indicates that the velocity of the positive ions is a linear function of the density of ionisation along the path of the electron beam.

(5) *Relation between Velocity of Ions and Electron Beam Current.*—As would be expected from the above results the velocity of the ions depends not only upon the velocity of the primary electrons but also upon the current in the electron beam. With the velocity of the electrons kept constant at 104 volts, seven velocity distribution curves were taken for different values of the current in the electron beam. In fig. 8 the mean velocities of the positive ions determined from these velocity distribution curves are plotted as ordinates against the current in the electron beam in microamps. It will be seen that the relation is a linear one within the experimental error, so confirming the conclusion arrived at above that the velocity of the positive ions is a linear function of the density of ionisation along the path of the electron beam.

Discussion of Results.

Before proceeding to discuss these results we shall briefly summarise the experimental data given above :—

- (a) The positive ions all move at right angles to the direction of the electron beam.
- (b) The intensity of the positive ion current and the mean velocity of the ions are both linear functions of the density of ionisation along the path of the electron beam, within the range investigated.

Langmuir and Mott-Smith* have shown that in a strongly ionised gas there are approximately equal numbers of electrons and positive ions, and that the electrons are moving in random directions with a Maxwellian velocity distribution. A difference of potential will be set up between any two regions in which the concentration of electrons is different, and we may apply the Boltzmann equipartition theorem to determine the magnitude of this potential difference. It is well known that in the positive column of a gas discharge, both longitudinal and radial potential gradients are set up, and Langmuir has ascribed the cause of these to variations in the concentration of ions and electrons in different regions of the positive column. Killian† has recently investigated the variation in electron concentration in the positive column of an electric discharge in mercury vapour, and has shown that such concentration gradients exist, and that they are of the right magnitude to account for the radial and longitudinal potential gradients found in the uniform positive

* 'Gen. Elec. Rev.,' vol. 27, pp. 449, 536, 616, 762, 810 (1924); 'Phys. Rev.,' vol. 26, p. 585; vol. 28, p. 727 (1926).

† Killian, 'Phys. Rev.,' vol. 35, p. 1238 (1930).

column. It appears that similar considerations can be applied to explain the results described in this paper.

In order to test this theory a Langmuir probe was inserted, and the electron concentrations measured at several different points along an axis at right angles to the electron beam. The necessary modification to the apparatus is shown in fig. 9. This figure shows a section of the apparatus in a plane at right angles

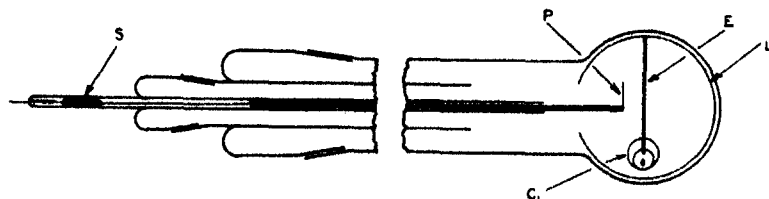


FIG. 9.—Showing Langmuir Probe Electrode.

to that shown in fig. 2. The probe, P, which consisted of a wire 0.5 mm. in diameter, had an exposed length of 9 mm. At the point where it emerged from the glass shielding tube it was bent so as to be parallel to the electron beam E. It could be moved along an axis at right angles to the electron beam by the action of a small electromagnet on the soft ion attachment, S. As before, the large shielding cylinder, L, lining the tube was connected directly to the anode, C₁, of the electron gun. The probe, P, was connected through a galvanometer to a potentiometer, the other side of which was connected to the anode of the electron gun.

PART II.

Determination of the Variation in Electron Concentration by a Langmuir Probe.

When the probe is negative with respect to the ionised gas, it repels electrons and attracts positive ions. The probe thus becomes covered with a positive ion sheath across which the whole drop in potential between it and the ionised gas is concentrated. Langmuir* has shown that when electrons are being collected in a retarding field, the electron current per square centimetre, I_e , to the collector is given by

$$I_e = i_e \frac{V^2}{e^2 T}, \quad (1)$$

where i_e is the random electron current density in the ionised gas outside the sheath, and V is the fall in potential across the sheath. The electrons in the

* Langmuir, *loc. cit.*

ionised gas have a Maxwellian velocity distribution corresponding to the temperature T . From (1) it is seen that

$$\frac{d}{dV}(\log I_e) = \frac{e}{kT}. \quad (2)$$

Thus if the logarithm of the electron current to a negatively charged collector is plotted against the potential of the collector a straight line should be obtained, whose slope is a measure of the temperature of the random moving electrons in the ionised gas. If V is expressed in volts the value of e/k is 11,600 degrees absolute per volt.

Equation (1) is true only so long as the probe is negative with respect to the gas, for when the probe is positive it is covered with an electron sheath. The electrons are then collected in an accelerating field, and I_e increases with V more slowly and according to different laws. Thus in the semi-logarithmic plot a straight line is obtained up to the space potential, after which a change in the slope of the curve should occur. When this change in slope is abrupt, the space potential can be fixed to within a few tenths of a volt.

At the space potential there is no sheath on the probe, and the value of I_e at this potential, therefore, gives by equation (1) the random electron current density, i_e , in the undisturbed gas. The concentration of electrons, n_e , is then obtained from the equation

$$n_e = \sqrt{\frac{2\pi m}{kT}} \cdot \frac{i_e}{e} = 4.03 \times 10^{13} \frac{i_e}{\sqrt{T}}, \quad (3)$$

where i_e is in amperes per square centimetres.

When cylindrical probes are used with low current densities, the radius of the sheath on the probe may be large compared with the radius of the probe itself. The current to the probe is then limited by orbital motion.* When this occurs the change in slope at the space potential in the semi-logarithmic plot of the current-voltage characteristic of the probe is not sufficiently abrupt to fix the space potential at all accurately. When the current to the probe is limited by orbital motion the problem may be treated as follows.

Langmuir and Mott-Smith have shown that when the electrons are being collected in an accelerating field, *i.e.*, when the probe is above the space potential

$$I_e^2 = \frac{4i_e^2}{\pi} \left(\frac{Ve}{kT} + 1 \right). \quad (4)$$

* Langmuir, 'Gen. Elec. Rev.', vol. 27, p. 616 (1924).

Therefore, if the square of the electron current per square centimetre received by the probe is plotted against the potential of the probe a straight line should be obtained. The intercept of this line on the V-axis is

$$V_0 = -kT/e = -T/11,600. \quad (5)$$

Thus if we know the temperature of the electrons which can be obtained from equation (2) we can find the space potential accurately from the I_e^2 , V plot.

The slope, S, of the line is from equation (4)

$$S = 4i_e^2 e / \pi kT \quad (6)$$

from which can be obtained the random electron current density

$$i_e = \sqrt{\pi kST/4e} = 8.22 \times 10^{-3} \sqrt{S \cdot T}. \quad (7)$$

By combining this with equation (3) the concentration of electrons, n_e , is then given by

$$n_e = 3.32 \times 10^{11} \sqrt{S}, \quad (8)$$

where $\sqrt{S}$ is expressed in amperes per square centimetre per volt[†].

Results.

Complete current-voltage characteristics were taken for seven different positions of the probe. On plotting the logarithm of the electron current to the probe against the potential of the probe relative to the anode of the electron gun, a very good straight line was obtained up to the space potential for all seven characteristics. A typical semi-log plot is shown in fig. 10, curve 1. The position of the probe in this instance was 6 mm. from the electron beam. The temperature of the electrons, obtained by equation (2) from the slope of the straight portion of the curve which was the same for all positions of the probe, is 21,200° K. This corresponds to 1.83 volts.

Owing to the very gradual change of slope at the space potential the latter cannot be determined from the semi-log plot with any great degree of accuracy. It may, however, be found far more accurately from an I_e^2 , V plot. On plotting the square of the electron current to the probe against the potential of the probe relative to the anode of the electron gun a good straight line was obtained for all positions of the probe. A typical I_e^2 , V plot obtained when the probe was 6 mm. from the electron beam is shown in fig. 10, curve 2. It should be noted that in fig. 10 I_e is the actual electron current received by the probe and not the current per square centimetre. In calculating the electron

concentrations from equations (3) and (8) the value of I_e in fig. 10 must be divided by the surface area of the probe, which is 0.282 sq. cm.

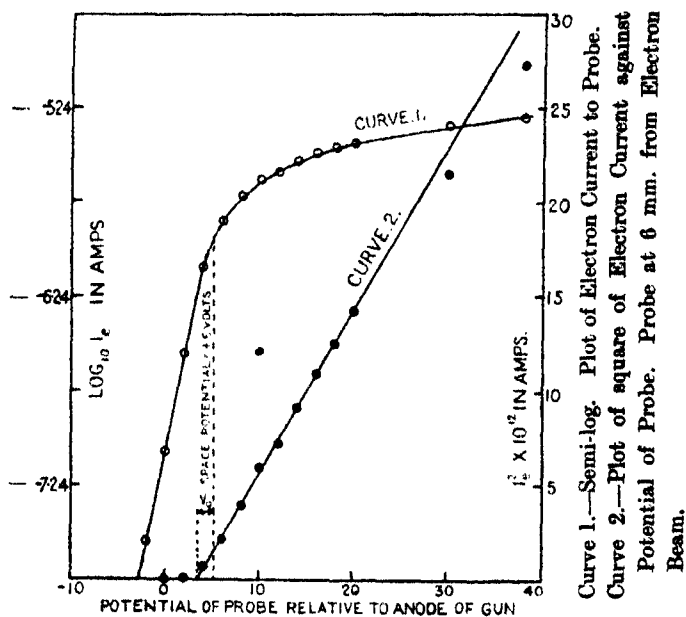


FIG. 10.

The space potential is obtained accurately from curve 2, fig. 10, by the use of equation (5) which gives $V_0 = 1.83$ volts, T being determined from curve 1. It will be seen from the figure that the space potential determined from curve 2 falls within the limits that are estimated from the kink in the semi-logarithmic plot shown in curve 1. This fact together with the general agreement shown in Table I between the values of n_e found by the two different methods justifies the assumption tacitly made above that the electron current to the probe is limited by orbital motion.

The values of i_e and n_e are obtained from the slope of the I_e^2, V curves by equations (7) and (8) respectively. These values are tabulated in columns 3 and 5 of Table I. The values of i_e obtained from the semi-logarithmic plots and the corresponding values of n_e obtained by equation (3) are given in columns 2 and 4.

Table I.—Potential difference between filament and anode of electron gun = 123 volts.

Electron beam current = 6.4 micro-amps.

Surface area of probe = 0.282 sq. cm.

Temperature of electrons, $T_e = 21,200^\circ \text{K}$.

Gas : mercury vapour at room temperature of 19.4°C .

1	2	3	4	5
Distance of probe from electron beam.	i_e from semi-log. plot.	i_e from I_e^2 , V plot.	n_e from semi-log. plot.	n_e from I_e^2 , V plot.
mm.	micro-amps. per sq. cm.	micro-amps. per sq. cm.	$\times 10^{-6}$.	$\times 10^{-6}$.
In beam	5.06	4.56	1.64	1.26
3	4.51	4.02	1.24	1.11
6	3.90	3.94	1.08	1.08
9	3.50	3.08	0.97	0.85
13	2.38	2.35	0.66	0.65
16	1.76	2.18	0.49	0.60
20	1.19	1.67	0.33	0.46

The values of the electron concentrations obtained from the I_e^2 , V plots, which are considered to be more accurate than those obtained from the semi-logarithmic plots are plotted in fig. 11 against the distance from the electron beam. This figure shows the variation in electron concentration along an axis at right angles to the electron beam.

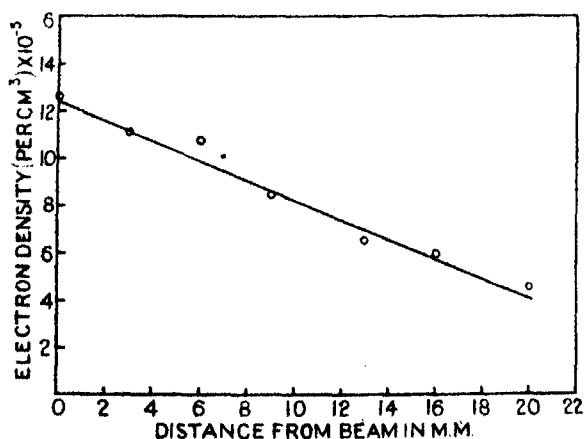


FIG. 11.—Relation between Electron Density and Distance from Electron Beam.

The distance from the electron beam to the slit in the cylinder C_2 (fig. 2) when the beam was set at 90° was 16 mm. The potential difference between the beam and the cylinder C_2 can now be determined from the Boltzmann equation,

$$n_1/n_2 = \frac{V_e}{\epsilon kT},$$

which gives

$$V = \frac{T}{11,600} \log_e \frac{n_1}{n_2}, \quad (9)$$

where n_1 and n_2 are the electron concentrations in the beam and at a point 16 mm. from the beam. The ratio of n_1 to n_2 obtained from fig. 11 is 2.17 which gives $V = 1.42$ volts. The directly measured velocity of the ions obtained from figs. 7 and 8 for an electron beam of this current and velocity is $V = 1.45$ volts.

Positive ions and slow electrons, the latter having a Maxwellian velocity distribution corresponding to a temperature of several thousand degrees absolute, diffuse out of the electron beam. Owing to the much greater mobility of the electrons a radial potential gradient will be set up around the electron beam in accordance with Poisson's equation. This potential gradient will tend to equalise the rates of diffusion of the electrons and positive ions by accelerating the positive ions out of the beam at right angles to it, and by altering the concentration of electrons around the beam in accordance with Boltzmann's equipartition theorem. When equilibrium is attained the concentration gradient in the electron gas around the beam will be such that it will give by means of the Boltzmann equation the resulting radial potential gradient around the electron beam.

The above case is exactly analogous to the calculation of the radial potential gradient in the positive column of an arc discharge by means of the Boltzmann equation, and the same arguments as are used by Langmuir and others to justify the use of this equation for such purposes are applicable.*

The results obtained with the probe, apart from demonstrating the existence of these radial concentration gradients, are in themselves interesting; for up to the present the use of probes has been restricted to investigations in gases where the random electron current density, i_e , is at least about a thousand times greater than it was in the above experiments. These results show that even at these low current densities the ultimate electrons in the plasma sur-

* See Langmuir, 'Gen. Elec. Rev.', vol. 27, p. 812 (1924); Langmuir, Fould and Dittmer, 'Science,' vol. 60, p. 392 (1924).

rounding the electron beam have a strictly Maxwellian velocity distribution, though it corresponds to a slightly lower temperature than is found with the much higher current densities that have hitherto been used.

The error introduced into experiments on the angular scattering of electrons in gases by a potential gradient at right angles to the electron beam will be treated in a separate paper.* It need only be stated here that the error introduced into the author's work† on this subject is negligible, though with more intense electron beams it might be quite considerable.

Summary.

An investigation of the fields set up by an electron beam in passing through an otherwise field-free enclosure is described. Two independent methods of investigation are employed: (a) measurement of the angular and velocity distributions of the positive ions generated along the path of the electron beam; and (b) measurement of the electron concentrations in a region around the electron beam by means of a Langmuir probe electrode.

The whole of the enclosure through which the electron beam passes is found to be filled with a gas of slow electrons having a Maxwellian velocity distribution corresponding to a temperature of several thousand degrees absolute.

Owing to concentration gradients in the electron gas, radial potential gradients exist around the electron beam which accelerate the positive ions, generated along its path, out at right angles to the beam. The intensity of the positive ion current and the mean velocity of the ions at a point outside the beam are both approximately linear functions of the density of ionisation along the path of the electron beam, within the range investigated.

In conclusion, I wish to express my thanks to Prof. Sir Ernest Rutherford for his constant help and encouragement, to Mr. P. M. S. Blackett for his interest and many helpful suggestions, and to Dr. M. L. E. Oliphant for many valuable discussions during the course of this work.

* 'Proc. Camb. Phil. Soc.,' *in press*.

† Arnot, 'Proc. Roy. Soc.,' A, vol. 125, p. 660 (1929).

*An Experimental Determination of the Intensity of Friction on the
Surface of an Aerofoil.*

By A. FAGE, A.R.C.Sc., and V. M. FALKNER, B.Sc.

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[PLATE 20.]

Introduction.

1. The principal part of the present investigation* is concerned with an experimental determination of the intensity of friction on the surface of an aerofoil from the well known relation $f = \mu (\partial V / \partial z)_{z=0}$, where f is the intensity of friction, μ the coefficient of viscosity, and V the velocity parallel to the surface at a normal distance z from the surface. In general, the velocity changes rapidly near the surface, so that the velocity gradient $(\partial V / \partial z)_{z=0}$ can only be predicted reliably when the velocity observations are taken very close to the surface. A review of the instruments available for the measurement of the velocity very close to a surface led to the conclusion that the most suitable device would be a surface tube of the type designed by Sir Thomas Stanton, and used to examine the conditions at the boundary of a fluid in turbulent motion.† The special feature of this tube is that the inner wall of the tube is formed by the surface itself. Three surface tubes were used in the present experiments, the widths of the openings being 0.0020, 0.0032 and 0.0044 inch respectively. These tubes were calibrated in the known laminar flow in a pipe with a rectangular cross-section, and with them it was possible to measure the velocity at points situated about 2 to 3 thousandths of an inch from the surface. The observations taken with the three tubes were found to be mutually compatible and allowed predictions to be made of the velocity gradients at the surface, and so of the frictional intensities. A check on the general accuracy of these values of frictional intensity was obtained from a comparison of the resultant frictional drag of the aerofoil predicted from them, with that obtained when the form drag

* The work described in this Paper was carried out in the Aerodynamics Department of the National Physical Laboratory, and permission to communicate the results was kindly granted by the Aeronautical Research Committee.

† 'Proc. Roy. Soc.,' A, vol. 97 (1920). By T. E. Stanton, Miss D. Marshall and Mrs. C. N. Bryant.

due to the normal pressures on the surface was subtracted from the total drag deduced from the total head losses in the wake. In addition, explorations of total head in the boundary layer, that is, the thin layer adjacent to the surface throughout which the retarding influence extends, were made with small tubes. It was found that the velocities measured near the surface with these tubes were compatible with those measured still closer to the surface with the surface tubes. The frictional drag of the aerofoil was also determined from the changes of momentum along the boundary layer.*

2. The experiments were made on a large model aerofoil mounted horizontally with very small clearances, between the vertical walls of a 7-foot wind tunnel. The observations were taken midway between the walls, where the flow was closely two-dimensional. To obtain a smooth surface in this region, the middle part (6-inch span) of the model was formed from a hollow gunmetal casting accurately milled to shape and polished. The remainder of the model was a light but stiff wooden framework built up of two longitudinal spars, nose and tail pieces, and transverse ribs, with a hand-finished surface covering of three-ply wood.

The section of the model was symmetrical and of the Joukowski type (see fig. 1). The chord was 39·7 inches and the maximum thickness of the section

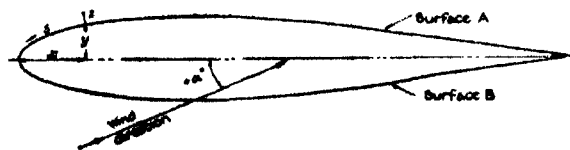


FIG. 1.—Aerofoil Section.

5·98 inches. Details of the construction of the model and also of the shape of the section are given later in § (28) and Table V.

3. *List of Symbols.*

V_0 ≡ Velocity of the undisturbed air stream relative to the model.

V ≡ Velocity at any point in the field.

p_0 ≡ Pressure in the undisturbed air stream.

p ≡ Pressure at any point in the field.

H_0 ≡ Total head in the undisturbed air stream.

H ≡ Total head at any point in the field.

* The observations given in the Paper have not been corrected for the interference of the tunnel walls on the flow around the aerofoil.

ρ $\equiv$ Density of the air.

μ $\equiv$ Coefficient of viscosity.

ν $\equiv$ Coefficient of kinematic viscosity.

K_D $\equiv$ Drag coefficient (drag per unit length/ ρCV_0^2).

x and y $\equiv$ Co-ordinates of a point on the surface of the aerofoil. The origin is taken at the nose of the section, and the axis OX along the chord.

z $\equiv$ Normal distance of a point from the surface.

δ $\equiv$ Thickness of the boundary layer, measured normal to the surface.

s $\equiv$ Peripheral distance of a point on the section measured from the nose.

$\bar{z}$ $\equiv$ Distance of the effective centre of a surface tube from the surface.

C $\equiv$ Chord of aerofoil section (39.7 inches).

A $\equiv$ Area.

f $\equiv$ Intensity of surface friction.

V_1 $\equiv$ Mean velocity in calibration pipe.

W $\equiv$ Width of the opening of a surface tube.

d $\equiv$ Depth of the section of the calibration pipe.

w $\equiv$ Width of the section of the calibration pipe.

Determination of the Intensity of Surface Friction (f) from the Relation

$$f = \mu \left(\frac{\partial V}{\partial z} \right)_{z=0}.$$

4. Sir Thomas Stanton* has shown that in turbulent motion in pipes there exists at the boundary, a layer of fluid in laminar motion, which has zero velocity at the boundary. The intensity of surface friction f is therefore given by $\mu \left(\frac{\partial V}{\partial z} \right)_{z=0}$ where the origin is taken in the boundary, z is measured along the normal, V is the velocity parallel to the boundary, and μ is the coefficient of viscosity of the fluid. This relation can be used to determine the surface friction from the shear in the fluid whether the general motion in the boundary layer is laminar or turbulent.

5. *Surface Tubes.*—It is apparent that to determine the value of $\left(\frac{\partial V}{\partial z} \right)_{z=0}$ it is essential to take measurements of velocity very close to the surface. To allow this to be done, Sir Thomas Stanton designed a special form of Pitot tube, which was such that the inner wall of the tube was formed by the surface itself, and for which the width of the opening could be varied by moving the outer wall. Tubes of a somewhat similar type have been used in the present experiments. A departure in design had, however, to be made, for since numerous observations had to be taken at different points on the surface,

* *Loc. cit.*

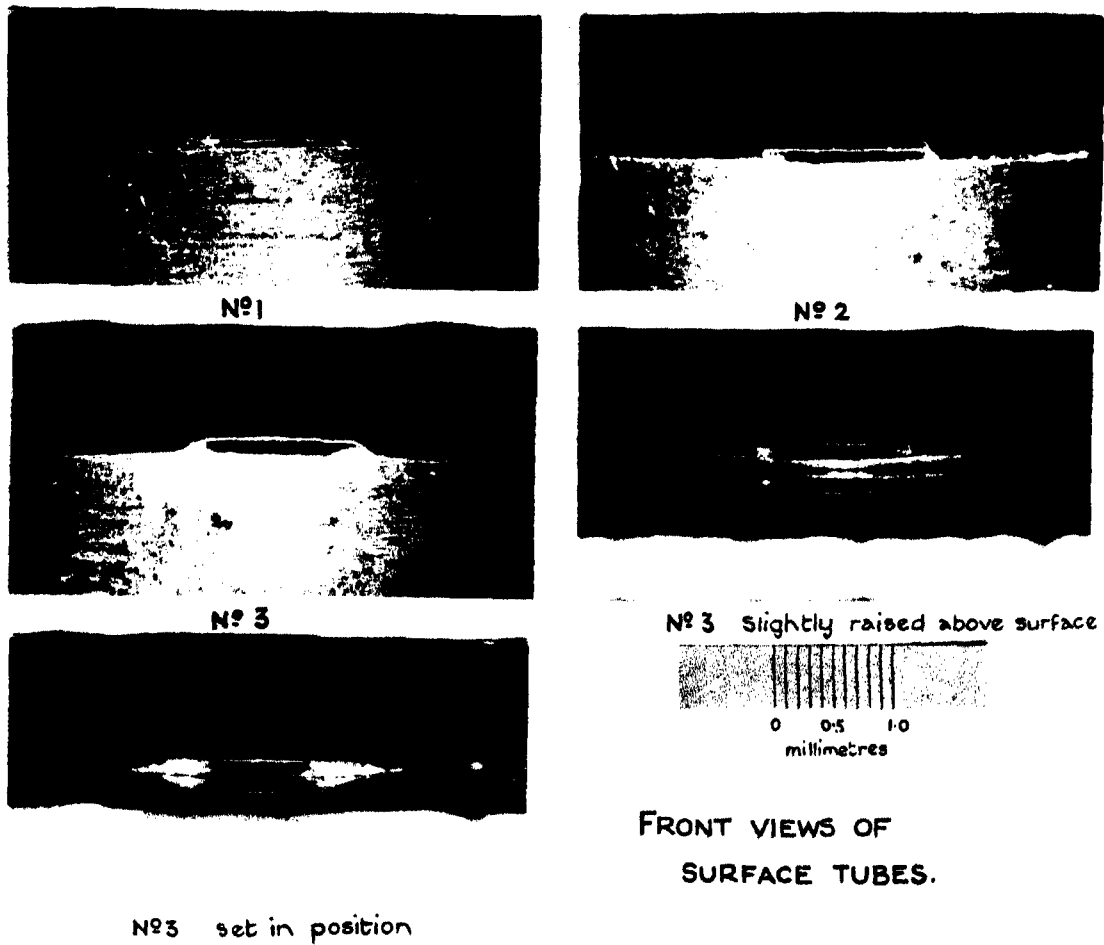


FIG. 3.

the labour involved in fitting a tube for which the opening could be varied at will would be excessive. It was decided therefore to use several tubes with very small fixed openings, each tube being constructed on the top of a circular rod of diameter 0.2 inch, designed to pass with a very small clearance through holes in the surface of the model, and to mount each tube so that the top surface of the rod was flush with the surface of the model. Three tubes of this type—designated hereinafter Surface Tubes Nos. 1, 2 and 3—were constructed, the widths of the openings being 0.0020, 0.0032, and 0.0044 inch respectively. The outer wall of each tube was formed by a thin steel cap, rectangular in plan form, ground at the front edge to a thickness of about 0.0006 inch. A hole of fine bore drilled along the axis of the rod served to transmit the pressure at the mouth of a tube to the manometer.

6. Great care was taken in setting a surface tube. The method of setting is illustrated in the diagrammatic sketch of fig. 2. A small reflecting glass

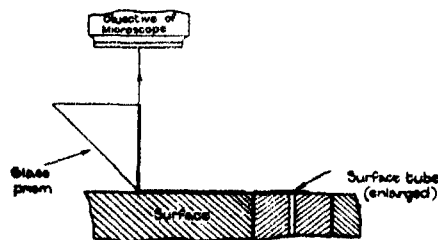


FIG. 2.

prism with a sharp edge in contact with the surface was used as a mirror to sight along the surface. The image obtained was viewed under a microscope (magnification 40). At the outset, the carrier rod was slowly lowered until its top surface was just above the surface of the aerofoil. The rod was then tapped until its front edge just disappeared. The top of the rod, and so the inner wall of the tube, was then flush with the surface. A check on the accuracy of mounting was obtained from a measurement of the width of the tube opening on a graticule carried in the eyepiece of the microscope. To obtain a clear image a beam of light from a Pointolite lamp was focussed on to the mouth of a tube. Two of the photographs in fig. 3 (Plate 20) show a tube just raised above the surface and also just mounted in place.* Photographs of the mouths of the three tubes are also shown. The device, mounted within the aerofoil, which held a surface tube in place is described later in § (20). This method of setting a surface tube was found to work satisfactorily in practice.

* Reflected images in the bright surface are also seen.

7. *Calibration of Tubes.*—It is known that when the opening of a surface tube is very small, the speed deduced from the pressure at the mouth is not the same as that at the geometrical centre of the opening. Each tube had therefore to be calibrated to determine the position of the "effective centre," corresponding to the speed deduced from the measured pressure. These calibrations were made in a long pipe of rectangular cross-section, which had laminar flow at the cross-section where a tube was placed. The mean flow and the velocity distribution at the wall were calculated from the measured pressure drop down the pipe. The information needed for the design of the calibration pipe was obtained from a paper by S. J. Davies and C. M. White,* on an experimental study of the flow of water in pipes of rectangular section. The relevant data taken from that paper are given in the curves of fig. 4.

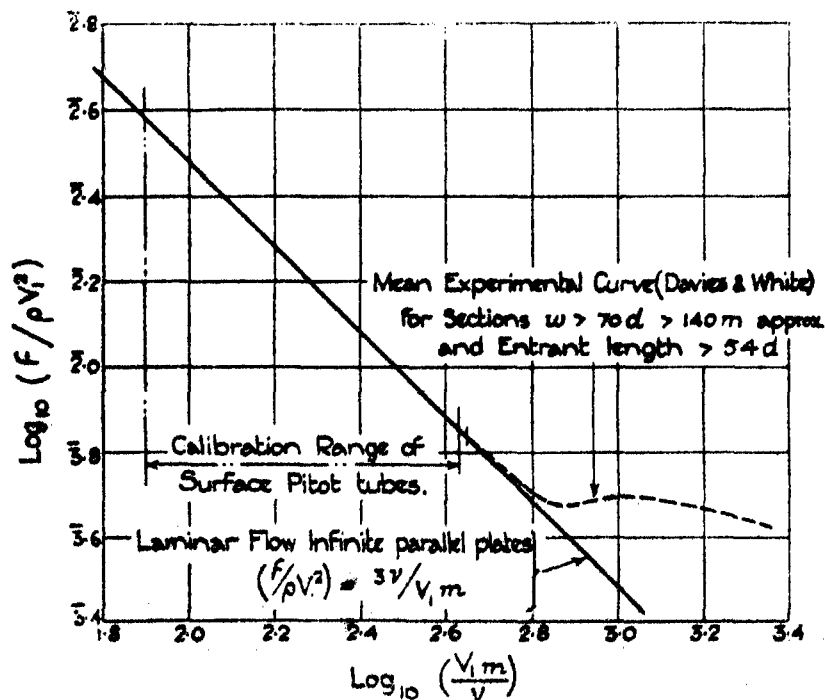


FIG. 4.—Resistance to Flow through Pipes of Rectangular Section.

They show that when the ratio of the width (w) to the depth (d) of the cross-section of a rectangular pipe exceeds 70, the coefficient of frictional resistance at a distance from the mouth greater than $54d$ has the same value as that for the laminar flow between infinite parallel plates at the distance (d) apart, provided

* 'Proc. Roy. Soc.,' A, vol. 119 (1928).

the value of (mV_1/ν) does not exceed 450 ($[\log_{10} (mV_1/\nu) = 2.65]$), where m is the hydraulic mean depth, that is the area of the section divided by the periphery, and V_1 is the mean rate of flow in the pipe.

8. The dimensions of the pipe used for the calibration of the surface tubes were:—Overall length 17.0 inches, width of the section 1.97 inches, depth of the section 0.0300 inch. Each tube was mounted on the centre line of one of the wider walls at a distance of 10 inches (entrant length $330d$), from the mouth, and calibrated over a speed range 10 to 54 ft./sec. $[\log_{10} (V_1m/\nu) = 1.9$ to $2.63]$. The conditions necessary for laminar flow were therefore satisfied, and the flow between the two wider walls could be taken as the same as the laminar flow between parallel plates of infinite extent at the distance d apart. The mean rate of flow down the pipe was therefore given by the expression $V_1 = fd/6\mu = (d^2/12\mu) \partial p/\partial l$, where $(\partial p/\partial l)$ was the pressure gradient down the pipe; and the distance $\bar{z}$ from the wall corresponding to a velocity V was given by the relation $\bar{z} = [1 - \sqrt{1 - (2V/3V_1)}] \cdot d/2$.

The determination of the effective distance $\bar{z}$ involved therefore only two measurements. First, that of the pressure drop $(\partial p/\partial l)$ from which the mean velocity V_1 was estimated; and, second, the difference between the pressure at the mouth of the surface tube and the static pressure in the pipe, from which the velocity V was deduced.

It should be added that a part (of length 12 inches) of the wall on which a tube was mounted was made detachable, to facilitate the mounting of the tube: that the air was sucked through the pipe by a centrifugal blower of the ordinary type: and that a few velocity observations taken with a small Pitot tube at the centre of the pipe were found to be in reasonably close agreement with those predicted from the pressure drop on the assumption that the flow was laminar.

9. The results obtained from several calibrations of each surface tube are given in fig. 5. Values taken from the curves in this figure are also collected in Table I, in a form which readily reveals some interesting characteristics of these tubes. Reference to this table shows that the effective centre of Tube No. 3 was within the opening and just beyond its geometrical centre, whereas the effective centre of Tube No. 1 was beyond the outer edge of the opening. The ratio of the effective distance $\bar{z}$ to the width of the opening W increased therefore as the width was decreased.* Table I also shows that there was a pronounced outward movement of the effective centre of each tube, as the speed at the mouth was decreased. But the most important

* See Stanton, *loc. cit.*

Table I.— $W \equiv$ Width of the Opening of a Tube.

Velocity calculated from the pressure at the mouth of the tube. V ft./sec.	Value of $\bar{z}$ (inches).		
	No. 3. $W = 0.0044$ inch (mean values).	No. 2. $W = 0.0032$ inch. Curve E.	No. 1. $W = 0.0020$ inch (mean values).
8	0.00320	0.00320	0.00270
11	0.00298	0.00296	0.00253
14	0.00281	0.00276	0.00238
17	0.00268	0.00258	0.00224
20	0.00255	0.00241	0.00217

characteristic exhibited in Table I, in so far as the present work was concerned, was that although the opening of Tube No. 1 was less than one-half of that of Tube No. 3, yet the effective distance was only about 15 per cent. smaller. Tube No. 1 with its smaller opening did not, therefore, allow observations to be taken much closer to the surface than either of the Tubes Nos. 2 and 3. Tube No. 1 was used to a very limited extent on the aerofoil.

In view of the tendency for the mouth of a tube to become partially blocked with fine dust, it was necessary on occasions to clean out the mouth, and, whenever this was done, the tube was re-calibrated. The results of these calibrations, and also the dates at which they were made, are given in fig. 5. The curves for Tube No. 3 show systematic changes with time; and it is not improbable that these changes are connected with small alterations in the shape of the mouth which occurred when it was cleaned.

The relatively large differences between the calibration curve E for Tube No. 2 and the curves F and G taken at earlier dates arise however from another cause. After this tube has been in use for some time a very small leak was discovered at an edge of the outer wall, and after this edge had been coated with "Newskin," the upper curve E was obtained. There was, however, no need to discard the observations taken on the aerofoil with this tube before the discovery of the leak, for the appropriate calibration of the tube for its condition at the time of observation was used to estimate the velocity at the surface. It may be concluded, however, that the curves given in fig. 5 clearly illustrate the need for frequent calibrations of this type of small surface tube.

Some values taken from the calibration curves obtained by Sir Thomas Stanton for a surface tube with a movable outer wall are plotted in fig. 5. These have the same character as those obtained for the tubes used in the

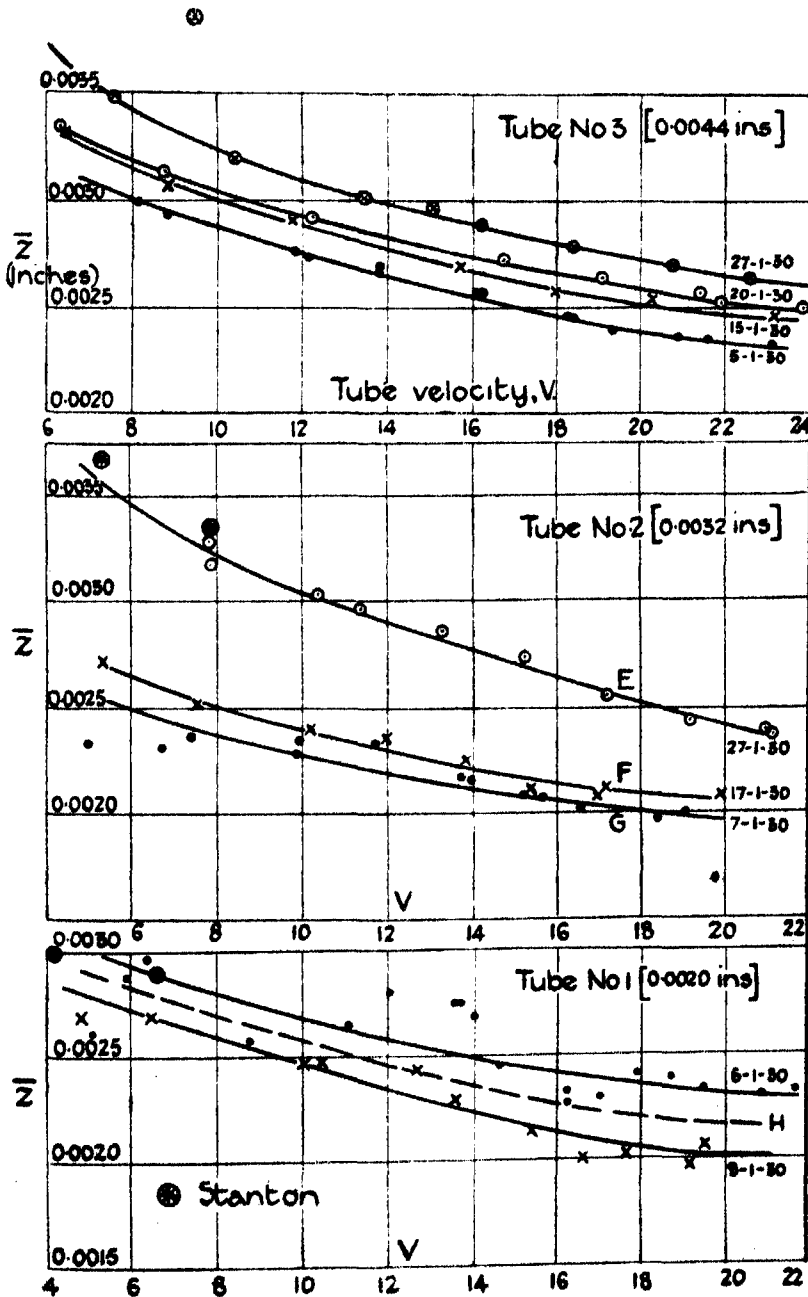


FIG. 5.

present experiments. A very close agreement between the two series of values would not be expected, since the tubes were not geometrically similar.

10. *Velocity near the surface.*—Measurements of velocity near the surface of the aerofoil were made with the surface tubes mounted at seventeen positions between $x = 0.0524 C$ and $x = 0.956 C$. As the aerofoil was symmetrical, the velocity measurements were taken on one surface only, referred to as surface "A," see fig. 1. The holes through which the carrier rods passed were carefully drilled normal to the surface, and near the median section of the gunmetal centre piece. These holes were reamed to a diameter which would just allow a rod to pass through with an exceedingly fine clearance. Static-pressure holes of small diameter were also drilled in a section situated at a small lateral distance from the median section. It was possible therefore to measure directly the difference between the pressure at the mouth of a surface tube and the corresponding static pressure at the surface. These pressure differences were measured on a 26-inch Chattock Tilting Gauge. Surface holes when not in use were plugged up with a preparation of wax and resin, scraped to the contour of the metal surface.

Measurements of the velocity near the surface A were made at a wind speed of 60 ft./sec., with the aerofoil at incidences -6.18° , -3.18° , -0.18° , 2.82° and 5.82° , and also at a wind speed of 80 ft./sec. with the aerofoil at -0.18° . To allow the general accuracy of observation to be assessed, the complete velocity results (time-average values) taken at $\alpha = -0.18^\circ$ for the speeds 60 and 80 feet per second are presented in Table II. It will be observed that the velocity results are arranged in pairs. The first value of each pair was obtained when the velocity of the general stream (V_0) was slowly increased to the steady value at which the measurement was made; whilst the second value was obtained when the general velocity was slowly decreased to the steady value. Of these two values, the first was always greater than the second. Mean values have, however, been taken, since at the speeds $V_0 = 60$ and 80 feet per second, the differences between the values of the pairs were not large, and since there was no reason to favour one value of a pair rather than the other.

With only a few exceptions, the velocities measured with the surface tubes lie between 7 and 20 ft./sec., that is, the velocity range covered in the calibrations of the tubes.

Values of the effective distance $\bar{z}$ are also given in Table II. The calibration curve of fig. 5, selected for the determination of $\bar{z}$, was the one taken at the date nearest to that at which the velocity measurements were made on the

Table II.—Values of $(f/\rho V_0^2)$, V , and $\bar{z}$. Surface A. $\alpha = -0.18^\circ$.
 $\bar{z} \equiv$ effective distance (inches).

(x/c).	Tube.	Calibration Curve.	Velocity, $V_0 = 60$ ft./sec.			Velocity, $V_0 = 80$ ft./sec.			
			V, ft./sec.	$\frac{(f \times 10^3)}{\rho V_0^2}$.	$(\bar{z} \times 10^3)$.	V, ft./sec.	$\frac{(f \times 10^3)}{\rho V_0^2}$.	$(\bar{z} \times 10^3)$.	
0.0167	2	E	$\left\{ \begin{smallmatrix} 13.0 \\ 12.2 \end{smallmatrix} \right\}$	12.6	$\left\{ \begin{smallmatrix} 2.37 \\ 2.38 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 18.6 \\ 18.3 \end{smallmatrix} \right\}$	18.5	$\left\{ \begin{smallmatrix} 2.24 \\ 2.22 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 2.49 \\ 2.73 \end{smallmatrix} \right\}$
	3	A	$\left\{ \begin{smallmatrix} 13.7 \\ 13.4 \end{smallmatrix} \right\}$	13.5	2.39	$\left\{ \begin{smallmatrix} 19.9 \\ 19.8 \end{smallmatrix} \right\}$	19.9	2.20	
0.0330	2	E	$\left\{ \begin{smallmatrix} 14.3 \\ 13.7 \end{smallmatrix} \right\}$	14.0	$\left\{ \begin{smallmatrix} 2.72 \\ 2.75 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 20.6 \\ 20.2 \end{smallmatrix} \right\}$	20.4	$\left\{ \begin{smallmatrix} 2.58 \\ 2.54 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 2.39 \\ 2.66 \end{smallmatrix} \right\}$
	3	A	$\left\{ \begin{smallmatrix} 15.3 \\ 15.1 \end{smallmatrix} \right\}$	15.2	2.77	$\left\{ \begin{smallmatrix} 21.9 \\ 22.1 \end{smallmatrix} \right\}$	22.0	2.50	
0.0504	1	H	$\left\{ \begin{smallmatrix} 11.2 \\ 9.6 \end{smallmatrix} \right\}$	10.4	$\left\{ \begin{smallmatrix} 2.17 \\ 2.53 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 16.0 \\ - \end{smallmatrix} \right\}$	16.0	$\left\{ \begin{smallmatrix} 2.12 \\ 2.39 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 2.28 \\ 2.00 \end{smallmatrix} \right\}$
	2	G	$\left\{ \begin{smallmatrix} 12.4 \\ 11.2 \end{smallmatrix} \right\}$	11.8	2.88	$\left\{ \begin{smallmatrix} 18.0 \\ 17.4 \end{smallmatrix} \right\}$	17.7	2.67	
	3	D	$\left\{ \begin{smallmatrix} 12.8 \\ 12.8 \end{smallmatrix} \right\}$	12.8	2.54	$\left\{ \begin{smallmatrix} 18.8 \\ 19.2 \end{smallmatrix} \right\}$	19.0	2.37	$\left\{ \begin{smallmatrix} 2.39 \\ 2.42 \end{smallmatrix} \right\}$
0.0756	2	G	$\left\{ \begin{smallmatrix} 10.5 \\ 8.5 \end{smallmatrix} \right\}$	9.5	$\left\{ \begin{smallmatrix} 2.21 \\ 2.19 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 14.8 \\ 14.4 \end{smallmatrix} \right\}$	14.6	$\left\{ \begin{smallmatrix} 2.11 \\ 2.13 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 2.08 \\ 2.48 \end{smallmatrix} \right\}$
	3	D	$\left\{ \begin{smallmatrix} 12.4 \\ 10.2 \end{smallmatrix} \right\}$	11.3	2.17	$\left\{ \begin{smallmatrix} 18.0 \\ 17.2 \end{smallmatrix} \right\}$	17.6	2.14	
0.1007	1	H	$\left\{ \begin{smallmatrix} 11.2 \\ 8.2 \end{smallmatrix} \right\}$	9.7	$\left\{ \begin{smallmatrix} 2.00 \\ 1.96 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 15.3 \\ 14.7 \end{smallmatrix} \right\}$	15.0	$\left\{ \begin{smallmatrix} 1.95 \\ 1.87 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 2.32 \\ 2.14 \end{smallmatrix} \right\}$
	2	G	$\left\{ \begin{smallmatrix} 9.9 \\ 8.1 \end{smallmatrix} \right\}$	9.0	2.07	$\left\{ \begin{smallmatrix} 13.7 \\ 12.9 \end{smallmatrix} \right\}$	13.3	1.87	
	3	D	$\left\{ \begin{smallmatrix} 10.1 \\ 9.3 \end{smallmatrix} \right\}$	9.7	1.80	$\left\{ \begin{smallmatrix} 14.8 \\ 14.8 \end{smallmatrix} \right\}$	14.8	1.70	$\left\{ \begin{smallmatrix} 2.14 \\ 2.62 \end{smallmatrix} \right\}$
0.1511	1	H	$\left\{ \begin{smallmatrix} 10.1 \\ 7.9 \end{smallmatrix} \right\}$	9.0	$\left\{ \begin{smallmatrix} 1.83 \\ 1.69 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 15.3 \\ 14.5 \end{smallmatrix} \right\}$	14.9	$\left\{ \begin{smallmatrix} 1.94 \\ 1.36 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 2.32 \\ 2.22 \end{smallmatrix} \right\}$
	2	G	$\left\{ \begin{smallmatrix} 9.2 \\ 5.8 \end{smallmatrix} \right\}$	7.5	1.69	$\left\{ \begin{smallmatrix} 11.8 \\ 10.6 \end{smallmatrix} \right\}$	11.2	1.36	
	3	D	$\left\{ \begin{smallmatrix} 8.8 \\ 8.4 \end{smallmatrix} \right\}$	8.6	1.56	$\left\{ \begin{smallmatrix} 13.5 \\ 13.5 \end{smallmatrix} \right\}$	13.5	1.52	$\left\{ \begin{smallmatrix} 2.22 \\ 2.68 \end{smallmatrix} \right\}$
0.2015	2	G	$\left\{ \begin{smallmatrix} 7.9 \\ 7.1 \end{smallmatrix} \right\}$	7.5	$\left\{ \begin{smallmatrix} 1.68 \\ 1.54 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 13.7 \\ 13.3 \end{smallmatrix} \right\}$	13.5	$\left\{ \begin{smallmatrix} 1.90 \\ 1.79 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 2.14 \\ 2.63 \end{smallmatrix} \right\}$
	3	D	$\left\{ \begin{smallmatrix} 8.2 \\ 7.6 \end{smallmatrix} \right\}$	7.9	1.40	$\left\{ \begin{smallmatrix} 14.9 \\ 14.3 \end{smallmatrix} \right\}$	14.6	1.68	
0.252	2	G	$\left\{ \begin{smallmatrix} 8.2 \\ 7.2 \end{smallmatrix} \right\}$	7.7	$\left\{ \begin{smallmatrix} 1.73 \\ 1.67 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 16.7 \\ 15.9 \end{smallmatrix} \right\}$	16.3	$\left\{ \begin{smallmatrix} 2.41 \\ 2.33 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 2.04 \\ 2.46 \end{smallmatrix} \right\}$
	3	D	$\left\{ \begin{smallmatrix} 9.0 \\ 8.8 \end{smallmatrix} \right\}$	8.9	1.61	$\left\{ \begin{smallmatrix} 18.3 \\ 18.3 \end{smallmatrix} \right\}$	18.3	2.24	
0.302	2	F	$\left\{ \begin{smallmatrix} 9.4 \\ 8.6 \end{smallmatrix} \right\}$	9.0	$\left\{ \begin{smallmatrix} 1.97 \\ 1.92 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 19.2 \\ 19.2 \end{smallmatrix} \right\}$	19.2	$\left\{ \begin{smallmatrix} 2.80 \\ 2.74 \end{smallmatrix} \right\}$	$\left\{ \begin{smallmatrix} 2.07 \\ 2.48 \end{smallmatrix} \right\}$
	3	C	$\left\{ \begin{smallmatrix} 10.4 \\ 10.2 \end{smallmatrix} \right\}$	10.3	1.86	$\left\{ \begin{smallmatrix} 21.9 \\ 22.1 \end{smallmatrix} \right\}$	22.0	2.68	

Table II—(continued).

(x/c) .	Tube.	Calibration Curve.	Velocity, $V_0 = 60$ ft./sec.			Velocity, $V_0 = 80$ ft./sec.		
			V, ft./sec.	$\frac{(f \times 10^3)}{\rho V_0^2}$.	$(\bar{z} \times 10^3)$.	V, ft./sec.	$\frac{(f \times 10^3)}{\rho V_0^2}$.	$(\bar{z} \times 10^3)$.
0.353	2	F	$\left\{ \begin{array}{l} 12.3 \\ 11.5 \\ 14.1 \end{array} \right\}$	$\left\{ \begin{array}{l} 11.9 \\ 2.77 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.73 \\ 2.30 \end{array} \right\}$	$\left\{ \begin{array}{l} 22.6 \\ 22.2 \\ 26.1 \end{array} \right\}$	$\left\{ \begin{array}{l} 22.4 \\ 3.34 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.02 \\ 2.42 \end{array} \right\}$
	3	C	$\left\{ \begin{array}{l} 14.1 \\ 13.7 \end{array} \right\}$	$\left\{ \begin{array}{l} 13.9 \\ 2.69 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.77 \\ 2.77 \end{array} \right\}$	$\left\{ \begin{array}{l} 26.0 \\ 25.9 \end{array} \right\}$	$\left\{ \begin{array}{l} 3.29 \\ 3.24 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.42 \\ 2.42 \end{array} \right\}$
0.403	2	F	$\left\{ \begin{array}{l} 13.4 \\ 12.2 \end{array} \right\}$	$\left\{ \begin{array}{l} 12.8 \\ 3.05 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.93 \\ 2.26 \end{array} \right\}$	$\left\{ \begin{array}{l} 22.5 \\ 21.9 \end{array} \right\}$	$\left\{ \begin{array}{l} 22.2 \\ 3.29 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.04 \\ 2.43 \end{array} \right\}$
	3	C	$\left\{ \begin{array}{l} 14.5 \\ 14.3 \end{array} \right\}$	$\left\{ \begin{array}{l} 14.4 \\ 2.81 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.75 \\ 2.75 \end{array} \right\}$	$\left\{ \begin{array}{l} 25.1 \\ 24.9 \end{array} \right\}$	$\left\{ \begin{array}{l} 25.0 \\ 3.11 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.43 \\ 2.43 \end{array} \right\}$
0.504	2	F	$\left\{ \begin{array}{l} 13.1 \\ 12.1 \end{array} \right\}$	$\left\{ \begin{array}{l} 12.6 \\ 3.05 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.85 \\ 2.21 \end{array} \right\}$	$\left\{ \begin{array}{l} 19.3 \\ 19.1 \end{array} \right\}$	$\left\{ \begin{array}{l} 19.2 \\ 2.80 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.07 \\ 2.50 \end{array} \right\}$
	3	C	$\left\{ \begin{array}{l} 13.8 \\ 13.8 \end{array} \right\}$	$\left\{ \begin{array}{l} 13.8 \\ 2.65 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.79 \\ 2.79 \end{array} \right\}$	$\left\{ \begin{array}{l} 20.8 \\ 21.0 \end{array} \right\}$	$\left\{ \begin{array}{l} 20.9 \\ 2.52 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.50 \\ 2.50 \end{array} \right\}$
0.605	2	F	$\left\{ \begin{array}{l} 12.0 \\ 11.2 \end{array} \right\}$	$\left\{ \begin{array}{l} 11.6 \\ 2.70 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.61 \\ 2.31 \end{array} \right\}$	$\left\{ \begin{array}{l} 16.8 \\ 16.6 \end{array} \right\}$	$\left\{ \begin{array}{l} 16.7 \\ 2.38 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.12 \\ 2.54 \end{array} \right\}$
	3	C	$\left\{ \begin{array}{l} 13.3 \\ 13.1 \end{array} \right\}$	$\left\{ \begin{array}{l} 13.2 \\ 2.52 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.81 \\ 2.81 \end{array} \right\}$	$\left\{ \begin{array}{l} 19.4 \\ 19.4 \end{array} \right\}$	$\left\{ \begin{array}{l} 19.4 \\ 2.30 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.54 \\ 2.54 \end{array} \right\}$
0.706	2	F	$\left\{ \begin{array}{l} 11.4 \\ 10.2 \end{array} \right\}$	$\left\{ \begin{array}{l} 10.8 \\ 2.46 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.39 \\ 2.35 \end{array} \right\}$	$\left\{ \begin{array}{l} 16.5 \\ 16.1 \end{array} \right\}$	$\left\{ \begin{array}{l} 16.3 \\ 2.32 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.13 \\ 2.59 \end{array} \right\}$
	3	C	$\left\{ \begin{array}{l} 12.6 \\ 12.2 \end{array} \right\}$	$\left\{ \begin{array}{l} 12.4 \\ 2.32 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.86 \\ 2.86 \end{array} \right\}$	$\left\{ \begin{array}{l} 18.4 \\ 18.4 \end{array} \right\}$	$\left\{ \begin{array}{l} 18.4 \\ 2.15 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.59 \\ 2.59 \end{array} \right\}$
0.807	2	F	$\left\{ \begin{array}{l} 7.7 \\ 6.9 \end{array} \right\}$	$\left\{ \begin{array}{l} 7.3 \\ 1.54 \end{array} \right\}$	$\left\{ \begin{array}{l} 1.62 \\ 2.56 \end{array} \right\}$	$\left\{ \begin{array}{l} 11.7 \\ 11.7 \end{array} \right\}$	$\left\{ \begin{array}{l} 11.7 \\ 1.53 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.30 \\ 2.80 \end{array} \right\}$
	3	B	$\left\{ \begin{array}{l} 10.0 \\ 9.6 \end{array} \right\}$	$\left\{ \begin{array}{l} 9.8 \\ 1.70 \end{array} \right\}$	$\left\{ \begin{array}{l} 1.62 \\ 3.07 \end{array} \right\}$	$\left\{ \begin{array}{l} 14.6 \\ 14.6 \end{array} \right\}$	$\left\{ \begin{array}{l} 14.6 \\ 1.57 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.80 \\ 2.80 \end{array} \right\}$
0.868	2	F	$\left\{ \begin{array}{l} 7.5 \\ 6.5 \end{array} \right\}$	$\left\{ \begin{array}{l} 7.0 \\ 1.46 \end{array} \right\}$	$\left\{ \begin{array}{l} 1.54 \\ 2.58 \end{array} \right\}$	$\left\{ \begin{array}{l} 11.6 \\ 10.8 \end{array} \right\}$	$\left\{ \begin{array}{l} 11.2 \\ 1.44 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.35 \\ 2.84 \end{array} \right\}$
	3	B	$\left\{ \begin{array}{l} 9.5 \\ 9.3 \end{array} \right\}$	$\left\{ \begin{array}{l} 9.4 \\ 1.62 \end{array} \right\}$	$\left\{ \begin{array}{l} 1.54 \\ 3.10 \end{array} \right\}$	$\left\{ \begin{array}{l} 13.9 \\ 13.9 \end{array} \right\}$	$\left\{ \begin{array}{l} 13.9 \\ 1.47 \end{array} \right\}$	$\left\{ \begin{array}{l} 2.84 \\ 2.84 \end{array} \right\}$
0.956	3	A	$\left\{ \begin{array}{l} 8.1 \\ 7.5 \end{array} \right\}$	$\left\{ \begin{array}{l} 7.8 \\ 1.22 \end{array} \right\}$	$\left\{ \begin{array}{l} 3.45 \\ 3.45 \end{array} \right\}$	$\left\{ \begin{array}{l} 11.9 \\ 13.9 \end{array} \right\}$	$\left\{ \begin{array}{l} 12.9 \\ 1.27 \end{array} \right\}$	$\left\{ \begin{array}{l} 3.06 \\ 3.06 \end{array} \right\}$

The first value of V was measured when the tunnel speed was slowly increased to its steady value; and the second value when the tunnel speed was slowly decreased to its steady value.

aerofoil. The values of $\bar{z}$ are seen to be very small, and almost all of them lie between 2 and 3 thousandths of an inch.

It should be added that experiments were made at the tunnel speeds of 60 and 80 feet per second only, because the definite impression was formed that reliable accuracy would only be obtained with a small surface tube, when the pressure to be measured was not too small.

11. *The intensity of surface friction.*—It has just been shown that measure-

ments of velocity have been made very near the surface at normal distances $\bar{z}$ of 2 to 3 thousandths of an inch. The intensity of surface friction has been estimated from these results on the assumption that the velocity increases linearly from the zero value at the surface to the value V measured at the small distance $\bar{z}$. The intensity of surface friction is then given by the relation $f = \mu (V/\bar{z})$. Evidence will be given later to show that this assumption of linearity cannot be very far from the truth. The value of μ taken was 3.82×10^{-7} (slug-feet sec. units), which was the mean value for the temperature range (19.5°C. to 22.5°C.) covered in the experiments.

The values of $(f/\rho V_0^2)$ estimated from the velocity observations taken on the aerofoil at -0.18° incidence are given in Table II. An examination of these results shows that the values for Tube No. 2 tended to be slightly greater than those for Tube No. 3, but in general the agreement between the two series of values was close; and also that the few values for Tube No. 1 did not greatly differ from those for either Tube No. 2 or Tube No. 3. Accordingly, the means of the values of $(f/\rho V_0^2)$ for the three tubes were taken. Except in a few cases, an individual value differed from its mean value by less than ± 6 per cent.

12. The distributions of surface friction over surface A at incidences -6.18° , -3.18° , -0.18° , 2.82° and 5.82° are shown in figs. 6-8. It will be noticed (see fig. 1) that since the section is symmetrical the frictional curves measured on surface A at a negative incidence can be taken as those for the under surface of the aerofoil at a positive incidence. The curves in fig. 7 do not therefore differ greatly from those for the upper and under surfaces of the aerofoil at 3° . The experiments were in fact conducted at nominal incidences of $\pm 3^\circ$, but a correction of -0.18° had to be applied afterwards. Similarly the curves in fig. 8 are not greatly different from those for the upper and under surfaces of the aerofoil at an incidence of 6° .

Reference to figs. 6-8 shows that the frictional curves for the upper surface (surface A at a positive incidence) have two maxima, one situated near the nose and the other, a greater one, some distance beyond the first. As the incidence is increased both maxima become greater and they move towards the nose. The curves for the under surface (surface A at a negative incidence) also have two maxima, but they are smaller than those for the upper surface and move towards the tail as the incidence is increased. Measurements of the velocity distribution in the boundary layer (see later) suggest that a transition from laminar to turbulent flow takes place in the part of the boundary layer situated between the two maxima. The first maximum is therefore

associated with laminar flow, and the second with turbulent flow in the boundary layer. It must, however, be mentioned that it was noticed when taking observations of pressure at the nose of the aerofoil that the motion

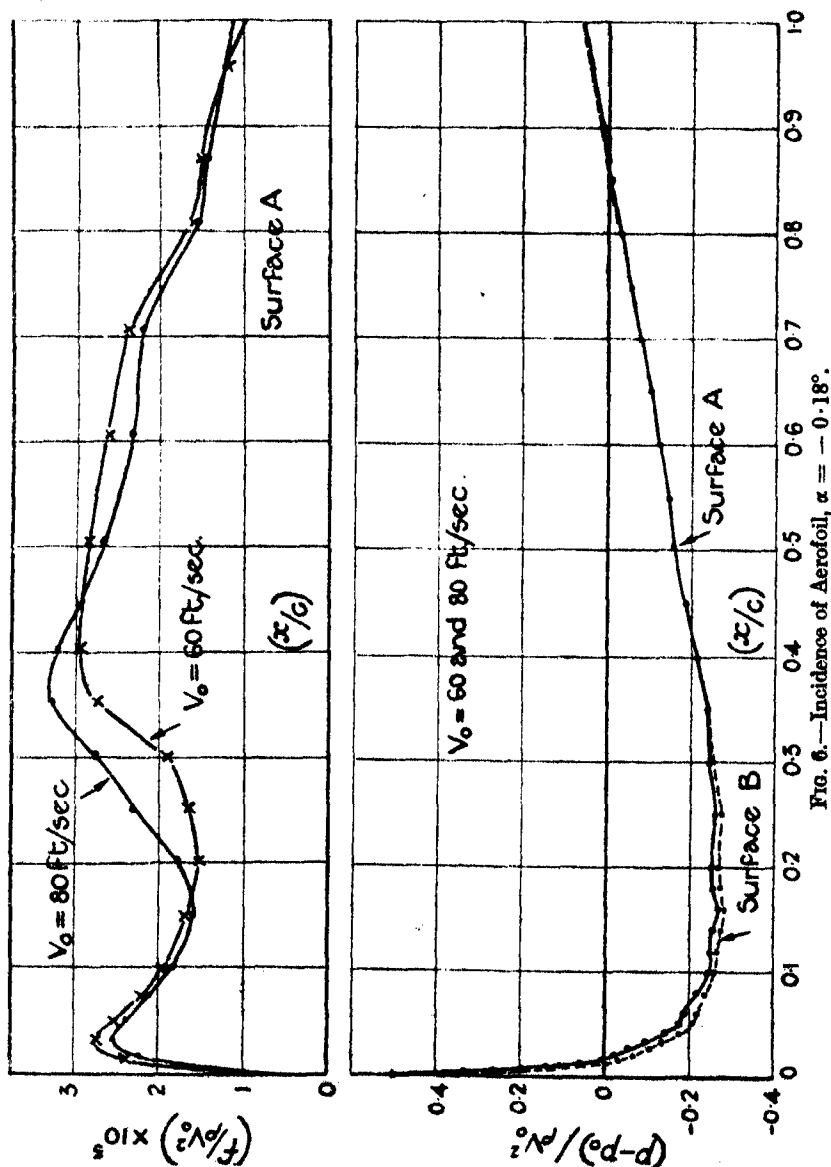


FIG. 6.—Incidence of Aerofoil, $\alpha = 0.18^\circ$.

was disturbed, and it is doubtful whether in this limited region the flow was laminar.

Another feature exhibited in the figs. 6-8 is that beyond the second maxi-

mum, on either the upper or the lower surface, the frictional intensity steadily falls with the distance from the nose. The frictional intensity does not,

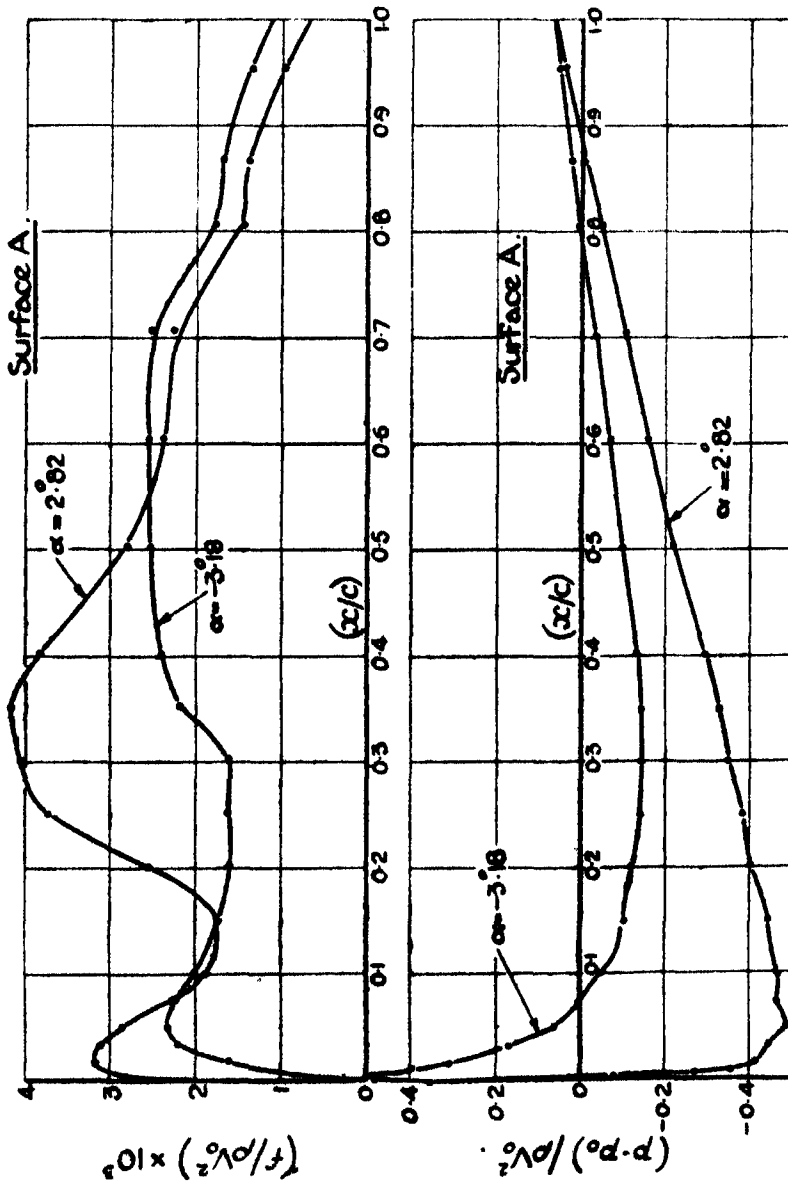


FIG. 7.

however, fall to zero on any part of the surface, even on the tail of the aerofoil at 5.82° incidence.

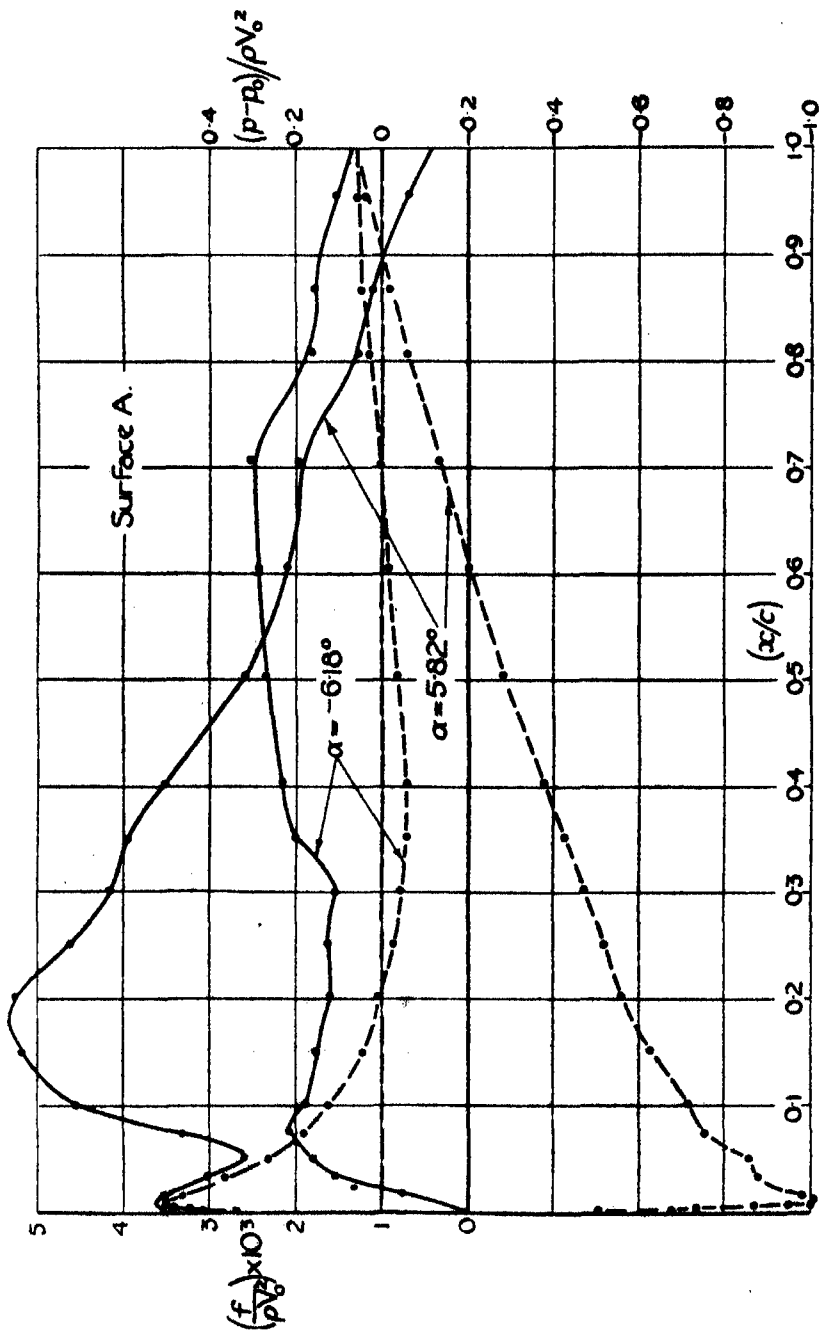


FIG. 8.

13. Values of $\int_{x=0}^{x=C} (f/\rho V_0^2 C) ds$, that is the integral taken over the surface of the frictional intensities, and also of $\int_{x=0}^{x=C} (f/\rho V_0^2 C) dx$, that is the force parallel to the chord due to the friction on the surface, are given in Table III. As would be anticipated from the shape of the surface, the values of the first series (Col. *a*) are only slightly greater (about 2 per cent.) than those of the second series (Col. *b*). The frictional force parallel to the chord (Col. *b*) is seen to increase with incidence. The rate of increase is much greater at a positive incidence than at a negative incidence.

Table III.—*Surface A.*

Angle of Incidence. α° .	V_0 ft. per sec.	$10^3 \int_{x=0}^{x=C} (f/\rho V_0^2 C) ds$.	$10^3 \int_{x=0}^{x=C} (f/\rho V_0^2 C) dx$.
-6.18 -3.18 -0.18 2.82 5.82 } 60 } (Column <i>a</i>.) 1.97 2.06 2.15 2.50 2.81 (Column <i>b</i>.) 1.96 2.02 2.10 2.45 2.79			
-0.18	80	2.20	2.16

The frictional drag of the aerofoil can be predicted from the values given in Col. *b* of Table III, for at a small angle of incidence the frictional drag has almost the same value as the frictional force acting parallel to the chord. Values of the frictional drag coefficient obtained in this manner for incidences of -0.18° , 2.82° and 5.82° , are given in Table IV. It is there seen that

Table IV.

V_0 ft./sec.	α°	Contribution to frictional drag coefficient.		Frictional drag coefficient.
		Surface A.	Surface B.*	
60	-0.18	0.00210	0.00215	0.00425
	2.82	0.00245	0.00205	0.00460
	5.82	0.00280	0.00195	0.00475
80	-0.18	0.00215	0.00220	0.00435

* These values were obtained by interpolation from the values for Surface A at a negative incidence.

the frictional drag coefficient increases slowly with incidence from 0.00425 at $\alpha = -0.18^\circ$ to 0.00475 at $\alpha = 5.82^\circ$; and also that the upper surface makes a greater fractional contribution to the frictional drag of the aerofoil, as the incidence is increased.

Measurement of the frictional drag of the aerofoil at $\alpha = -0.18^\circ$.

14. It is known that the frictional drag of an aerofoil can be determined by subtracting the form drag, that is the drag due to the normal pressures on the surface, from the total drag. An estimate of the frictional drag of the aerofoil at $\alpha = -0.18^\circ$ has been obtained in this manner, and compared with that predicted from the frictional intensities ($f/\rho V_0^2$) given in Table II.

15. *Total drag.*—The total drag was estimated from the integral of the total-head losses measured in the wake behind the median section of the metal centre piece. This method was used in preference to that of direct measurement, because the latter method would have involved the measurement of the drag of the composite model, with wooden and metal surfaces of different texture, whereas it was the drag of that part of the model with the metal surface that was needed. It was also known from some earlier experiments* that the results obtained by the total-head method would be in close agreement with those obtained by direct measurement.

The total-head losses were estimated from explorations of total head taken along lines normal to the undisturbed stream and situated at distances 1.1 C. behind the trailing edge, and 0.6 C. in front of the leading edge of the aerofoil. Curves of the total-head losses are given in fig. 9. The values of K_D determined from the areas of these diagrams are given on the diagrams. The drag coefficient of the aerofoil at an incidence of -0.18° is seen to be 0.0054.†

16. *Pressure experiments.*—Experiments were undertaken to measure the pressure distributions (a) around a section of the aerofoil at an incidence of -0.18° , for the speeds 60 and 80 ft./sec.; and (b) over the surface A at incidences of -6.18° , -3.18° , -0.18° (a repeat measurement), 2.82° and 5.82° , for the wind speed 60 ft./sec. In experiments (a), the pressure was measured at 39 holes drilled through the upper surface and the same number through the lower surface. In experiments (b), the pressure was measured at the 17 holes used in the experiments of §10, and in addition at the first

* Experiments on a Series of Symmetrical Joukowski Sections. By Fage, Falkner and Walker. Aeronautical Research Committee, R. and M. 1241 (Table II).

† The drag coefficient in an infinite stream would be about 0.0052; see R. and M. 1241.

10 holes (at the nose) used in experiments (a). The pressure at each hole was measured on a 26-inch Chattock Tilting Gauge against the static pressure (p_0) in the undisturbed wind. The experiments were made at nominal

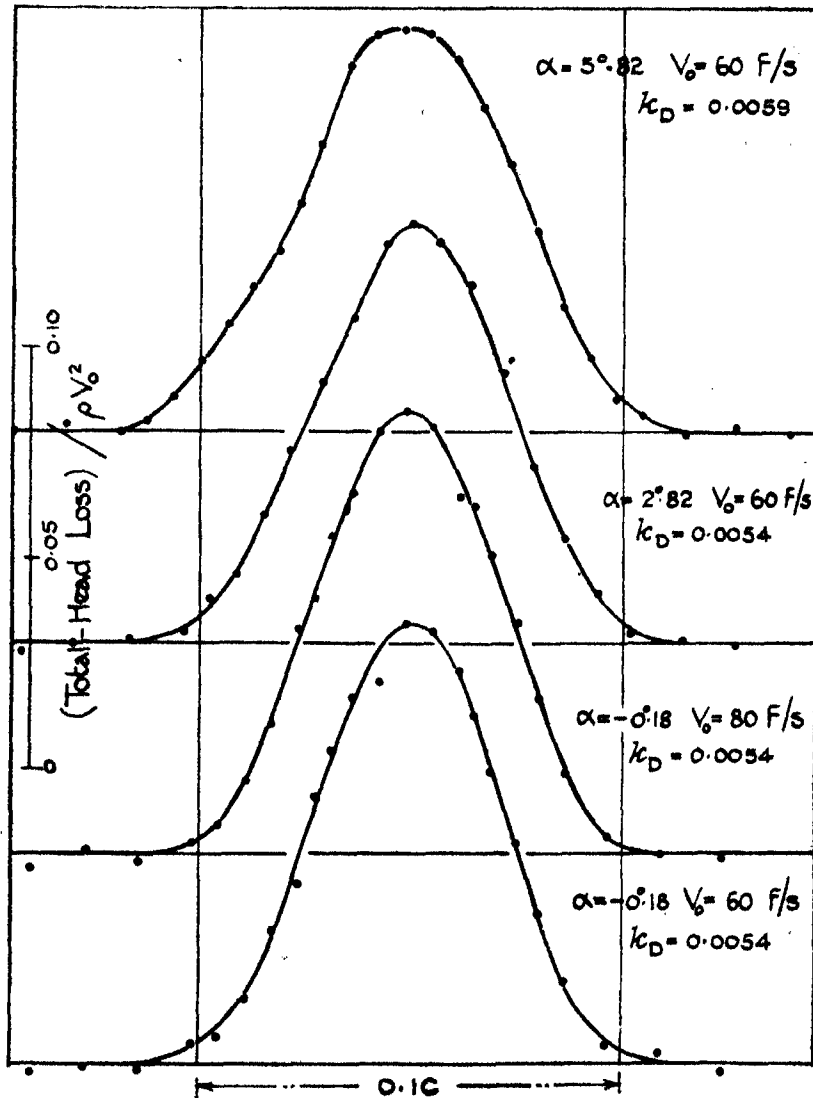


FIG. 9.—Curves of Total-head Losses in the Wake.

incidences of -6° , -3° , 0° , 3° and 6° . An analysis of all the pressure observations showed that at a nominal incidence of 0° , the true incidence was -0.18° . This correction was therefore applied to the nominal values of incidence.

The pressure results from the two series of experiments, expressed as non-dimensional coefficients $(p - p_0)/\rho V_0^2$, are collected in Tables V and VI. The curves obtained by plotting values of $(p - p_0)/\rho V_0^2$ against x/C are given in figs. 6-8. The general features of these curves are commonplace, and no discussion of them is needed. Attention must, however, be directed to the

Table V.—Values of $(p - p_0)/\rho V_0^2$.

Incidence = -0.18° . [Uncorrected for the interference of the tunnel walls.]

x/C .	y/C .	z/C .	Surface A.		Surface B.	
			$V_0 = 60.$	$V_0 = 80.$	$V_0 = 60.$	$V_0 = 80.$
0	0	0	0.504	0.502	0.504	0.503
0.0002	0.0025	0.0025	0.503	0.500	0.485	0.487
0.0008	0.0050	0.0051	0.477	0.472	0.442	0.438
0.0015	0.0073	0.0075	0.425	0.424	0.380	0.377
0.0027	0.0096	0.0101	0.381	0.378	0.326	0.326
0.0039	0.0118	0.0126	0.332	0.333	0.268	0.268
0.0053	0.0139	0.0151	0.265	0.262	0.207	0.206
0.0069	0.0159	0.0177	0.197	0.197	0.144	0.141
0.0085	0.0177	0.0201	0.140	0.139	0.088	0.083
0.0103	0.0195	0.0226	0.105	0.104	0.050	0.050
0.0123	0.0212	0.0252	0.061	0.059	+ 0.020	+ 0.021
0.0162	0.0243	0.0302	+ 0.007	+ 0.005	- 0.028	- 0.029
0.0204	0.0270	0.0352	- 0.020	- 0.022	- 0.069	- 0.066
0.0270	0.0308	0.0428	- 0.058	- 0.058	- 0.108	- 0.107
0.0337	0.0343	0.0504	- 0.100	- 0.099	- 0.138	- 0.141
0.0405	0.0375	0.0578	- 0.143	- 0.143	- 0.175	- 0.174
0.05	0.0413	0.0682	- 0.178	- 0.179	- 0.211	- 0.211
0.06	0.0448	0.0788	- 0.186	- 0.188	- 0.217	- 0.219
0.08	0.0508	0.0997	- 0.220	- 0.217	- 0.236	- 0.237
0.10	0.0559	0.1202	- 0.242	- 0.243	- 0.255	- 0.257
0.12	0.0601	0.1406	- 0.251	- 0.250	- 0.266	- 0.266
0.14	0.0636	0.1609	- 0.258	- 0.258	- 0.275	- 0.274
0.16	0.0664	0.1812	- 0.261	- 0.262	- 0.279	- 0.278
0.18	0.0687	0.2015	- 0.258	- 0.259	- 0.271	- 0.270
0.20	0.0706	0.2215	- 0.254	- 0.250	- 0.265	- 0.262
0.25	0.0741	0.2715	- 0.258	- 0.257	- 0.268	- 0.267
0.30	0.0753	0.3215	- 0.246	- 0.242	- 0.249	- 0.246
0.35	0.0750	0.3715	- 0.233	- 0.233	- 0.235	- 0.236
0.40	0.0733	0.4215	- 0.211	- 0.210	- 0.207	- 0.206
0.45	0.0702	0.4715	- 0.180	- 0.180	- 0.179	- 0.179
0.50	0.0663	0.5215	- 0.158	- 0.158	- 0.160	- 0.161
0.55	0.0617	0.5718	- 0.145	- 0.144	- 0.144	- 0.144
0.60	0.0559	0.6220	- 0.115	- 0.116	- 0.115	- 0.116
0.65	0.0498	0.6723	- 0.098	- 0.099	- 0.093	- 0.093
0.70	0.0433	0.7225	- 0.072	- 0.072	- 0.072	- 0.072
0.75	0.0365	0.7730	- 0.049	- 0.049	- 0.048	- 0.048
0.80	0.0292	0.8235	- 0.024	- 0.025	- 0.023	- 0.023
0.85	0.0218	0.8737	- 0.001	- 0.002	+ 0.005	+ 0.004
0.90	0.0150	0.9239	+ 0.018	+ 0.018	+ 0.024	+ 0.023
0.956	0.0077	0.9801	+ 0.047	+ 0.046	—	—

Radius at Nose = 0.0189 C.

Radius at Tail = 0.0025 C.

Table VI.—Values of $(p - p_0)/\rho V_0^2$.Surface A. $V_0 = 60$ ft./sec. [Uncorrected for the interference of the tunnel walls.]

x/C	y/C	$\alpha = 5.82^\circ$	$\alpha = 2.82^\circ$	$\alpha = -3.18^\circ$	$\alpha = -6.18^\circ$
0	0	- 0.101	0.377	0.333	- 0.172
0.0002	0.0025	- 0.302	0.275	0.426	+ 0.009
0.0008	0.0050	- 0.509	0.159	0.481	0.195
0.0015	0.0073	- 0.631	+ 0.048	0.504	0.337
0.0027	0.0096	- 0.677	- 0.015	0.507	0.411
0.0039	0.0118	- 0.731	- 0.074	0.501	0.448
0.0053	0.0139	- 0.870	- 0.194	0.481	0.482
0.0069	0.0159	- 0.950	- 0.273	0.457	0.499
0.0085	0.0177	- 1.005	- 0.330	0.420	0.504
0.0103	0.0195	- 1.009	- 0.359	0.396	0.500
0.0167	0.0245	- 0.988	- 0.416	0.310	0.468
0.0330	0.0340	- 0.873	- 0.447	0.168	0.361
0.0504	0.0417	- 0.859	- 0.487	0.069	0.264
0.0756	0.0495	- 0.753	- 0.463	+ 0.007	0.185
0.1007	0.0560	- 0.714	- 0.465	- 0.045	0.122
0.1511	0.0651	- 0.629	- 0.441	- 0.100	0.046
0.2015	0.0707	- 0.556	- 0.400	- 0.116	+ 0.010
0.252	0.0742	- 0.517	- 0.382	- 0.137	- 0.025
0.302	0.0753	- 0.472	- 0.350	- 0.140	- 0.041
0.353	0.0749	- 0.427	- 0.328	- 0.141	- 0.052
0.403	0.0731	- 0.379	- 0.294	- 0.130	- 0.052
0.504	0.0659	- 0.281	- 0.219	- 0.093	- 0.034
0.605	0.0553	- 0.202	- 0.156	- 0.064	- 0.017
0.706	0.0426	- 0.133	- 0.101	- 0.034	0
0.807	0.0281	- 0.060	- 0.040	+ 0.005	+ 0.028
0.868	0.0195	- 0.020	- 0.006	+ 0.027	0.043
0.956	0.0077	+ 0.031	+ 0.040	+ 0.053	0.057

curious waviness in these pressure curves, especially at the nose of the aerofoil. No explanation of this waviness can be offered. There were, however, good reasons to believe that it was not due to local irregularities, or to slight burrs at the edges of the pressure holes, for no irregularities on the metal surface could be detected either by touch or by measurement. Moreover, the waviness was observed on both the upper and lower surfaces, at all speeds and incidences; and also at two sections of surface A. It may be that the waviness arose from general disturbances in the wind of the tunnel, but no attempt was made to determine whether this was the cause.

17. *Form drag*.—The form drag of the aerofoil at $\alpha = -0.18^\circ$ was obtained directly from the area* of the diagrams obtained when the values of the pressure coefficient $(p - p_0)/\rho V_0^2$ for each surface were plotted against (y/C) . Although a large number of observations (37) was taken on each surface, it

* This area gives the longitudinal force, which can be taken as equal to the drag at an incidence of -0.18° .

was not possible to determine the form drag very accurately, for the pressure diagrams for each surface consisted of two loops of opposite sign, and the difference between the areas of these loops was small in comparison with the area of either loop. The mean value of K_D obtained from two estimations was 0.00145 for 60 feet per second and also for 80 feet per second. There may be an error between ± 10 per cent. in this estimated value of K_D . An error of this magnitude in the estimation of the form drag will give an error between ± 4 per cent. in the predicted value of frictional drag. The pressure data obtained from the experiments were not sufficient to allow the form drag at the incidences 2.82° and 5.82° to be predicted, for at these incidences only the pressure distributions over surface A were measured.

18. *Frictional drag.*—The value of the frictional drag coefficient obtained when the form drag coefficient was subtracted from the total drag coefficient was 0.00395 for the wind speed 60 ft./sec. and the same value for 80 ft./sec. The values of the coefficient of frictional drag obtained from the measured frictional intensities were 0.00425 ($V_0 = 60$) and 0.00435 ($V_0 = 80$) (see Table IV). The differences between the two sets of values are small, and amount to 0.0003 at 60 ft./sec. and 0.0004 at 80 ft./sec. There is therefore a close agreement between the values of the frictional drag obtained by the two entirely different methods. Evidence has therefore been obtained which indicates that, in general, the velocities measured with the small surface tubes are reliable, and also that the assumption made to predict the intensity of the surface friction—that is, that within 2 or 3 thousandths of an inch from the surface the velocity increases at a linear rate from the zero value at the surface—cannot be very far from the truth.

Explorations of Velocity in the Boundary layer ($\alpha = -0.18^\circ$).

19. Explorations of velocity were made near the Surface A of the aerofoil at an incidence of -0.18° for the two wind speeds 60 and 80 ft./sec. This work was undertaken to obtain some general information on the flow in the boundary layer, that is the thin layer which is retarded by the surface; and also because it was considered necessary to show that the velocities measured very close to the surface with the small surface tubes could be connected in a satisfactory manner with velocities measured at a greater distance from the surface. The additional velocity measurements have also allowed a third prediction of the frictional drag to be made from a consideration of the momentum and pressure changes in the boundary layer.

20. *Velocity experiments.*—The velocity distributions were predicted from

observations of total head taken with two small tubes, hereinafter referred to as Pitots A and B. The smaller Pitot A was used for the explorations made at the front part of the aerofoil, $x = 0.052$ C to 0.40 C, and the larger Pitot B for those at the rear part, $x = 0.5$ C to 0.956 C. Pitot A was constructed from a short length of fine hypodermic steel tube (external diameter 0.0197 inch), pressed at one end into a rectangular form, of external dimensions 0.029 inch $\times$ 0.010 inch (width). The width of the opening was 0.0024 inch. Pitot B was made from a tube of larger bore; the widths at the mouth being 0.0135 inch (external) and 0.0071 inch (opening). Each tube was mounted with its axis in the tangential direction, and with a longer side of the mouth parallel to the surface. At a distance of about one inch from the mouth, each tube had a right-angle bend, and the stem so obtained passed through a small hole in the aerofoil. This stem was soldered into a stiff cylindrical tube, which in turn was clamped to the screw of a standard micrometer. Attached to the nut of the micrometer was a wheel with 25 teeth, which was turned by a pawl controlled by an electromagnet.* By means of this device mounted within the aerofoil, the exploring tube could be moved outward from the surface in steps of about 0.001 inch.

A preliminary trial of the device showed that the reading of the micrometer scale did not give a sufficiently reliable measure of the distance of a tube from the surface when this distance was small. Calibrations of the micrometer scale were therefore made before and after each exploration of total head by measuring the distance of the centre of the mouth from the surface with a travelling microscope with cross-wires focussed on the mouth. To obtain clear definition, the mouth of the tube and the neighbouring surface was illuminated with a beam of light from a Pointolite lamp.

21. *Calibration of Pitot tubes.*—It is known that the pressure at the mouth of a very small Pitot tube differs from the total head in the airstream impinging on the mouth. Each of the Pitots A and B were therefore calibrated in a uniform wind, for the speed range covered in the aerofoil experiments. The observed values of $(2P/\rho V_0^2)$, where P is the excess of the pressure at the mouth of a Pitot over the total head in the wind, are given in Table VII. It is there seen that the value of P , and so the pressure at the mouth of a tube, depended on whether the speed of the tunnel wind had been raised or lowered to the steady value of observation; and that in general the observations of

* The electromagnet could not be accommodated within the aerofoil at the tail, and it was then necessary to mount the exploring tube on a device carried on the aerofoil surface.

pressure taken when the tunnel speed was raised to its steady value were greater than those taken when it was lowered to the steady value. The mean values of P were, however, small provided the velocity at the mouth of a Pitot was greater than about 30 ft./sec. Since almost all the velocities measured in the aerofoil experiments were greater than 30 ft./sec., it was decided that the corrections to be applied to the observations should be taken from the curves obtained when the mean values of P given in Table VII were plotted against V .

Table VII.—Calibration of Pitots A and B in a uniform wind.

P = excess of the pressure at the mouth of a Pitot over the total head in the wind.

The values given are the means from several calibrations.

Velocity, V , at the mouth of Pitot. ft./sec.	Values of $(2P/\rho V^2)$.		
	Pitot A.	Pitot B.	
80	$\begin{matrix} (a) & 0.020 \\ (b) & 0.015 \end{matrix} \left. \vphantom{\begin{matrix} (a) & 0.020 \\ (b) & 0.015 \end{matrix}} \right\} \begin{matrix} \text{Mean.} \\ 0.018 \end{matrix}$	$\begin{matrix} 0.008 \\ 0.008 \end{matrix} \left. \vphantom{\begin{matrix} 0.008 \\ 0.008 \end{matrix}} \right\} \begin{matrix} \text{Mean.} \\ 0.008 \end{matrix}$	(a) Tunnel speed slowly raised to its steady value.
60	$\begin{matrix} (a) & 0.018 \\ (b) & -0.013 \end{matrix} \left. \vphantom{\begin{matrix} (a) & 0.018 \\ (b) & -0.013 \end{matrix}} \right\} \begin{matrix} 0.003 \end{matrix}$	$\begin{matrix} 0.007 \\ 0.002 \end{matrix} \left. \vphantom{\begin{matrix} 0.007 \\ 0.002 \end{matrix}} \right\} \begin{matrix} 0.005 \end{matrix}$	(b) Tunnel speed slowly lowered to its steady value.
40	$\begin{matrix} (a) & 0.028 \\ (b) & -0.030 \end{matrix} \left. \vphantom{\begin{matrix} (a) & 0.028 \\ (b) & -0.030 \end{matrix}} \right\} \begin{matrix} -0.001 \end{matrix}$	$\begin{matrix} 0.011 \\ 0.004 \end{matrix} \left. \vphantom{\begin{matrix} 0.011 \\ 0.004 \end{matrix}} \right\} \begin{matrix} 0.008 \end{matrix}$	
22.5	$\begin{matrix} (a) & 0.040 \\ (b) & -0.096 \end{matrix} \left. \vphantom{\begin{matrix} (a) & 0.040 \\ (b) & -0.096 \end{matrix}} \right\} \begin{matrix} -0.028 \end{matrix}$	$\begin{matrix} 0.039 \\ -0.028 \end{matrix} \left. \vphantom{\begin{matrix} 0.039 \\ -0.028 \end{matrix}} \right\} \begin{matrix} 0.006 \end{matrix}$	

To determine to what extent the Pitots were suitable for observation in a region of steep velocity gradient, such as that near a surface, observations were taken with Pitot A mounted in the laminar flow adjacent to a wall of the pipe used in the earlier experiments described in § (8). The velocity gradient at the wall of the pipe was such that the theoretical velocity at the outer edge of the Pitot mouth was about 50 per cent. greater than that at its centre. The results of the calibration are given in Table VIII. They show that provided the velocity calculated from the pressure at the mouth exceeded 26.8 ft./sec.—the minimum velocity measured with the Pitot in the boundary layer of the aerofoil was about 30 ft./sec.—the effective centre was situated at a constant distance of about 0.0054 inch from the wall. The effective centre was therefore situated at a lateral distance of about 0.0005 inch from the

Table VIII.—Observations taken with Pitot A in the laminar flow at the wall of a pipe.

 $\bar{z}$ = distance of effective centre from wall.

V = velocity calculated from the pressure at the mouth of the Pitot tube.

Distance of the geometrical centre of the Pitot mouth from the wall was 0.0059 inch.

V. ft./sec.	Theoretical velocity at the outer edge of Pitot mouth.	$\bar{z}$ inches.
48.9	75.0	0.0053
37.5	56.8	0.0053
31.6	47.3	0.0054
26.8	39.6	0.0055

point ($z = 0.0059$ inch) which was taken as the geometrical centre of the mouth.* No corrections for "wall" interference were applied to the observations taken on the aerofoil with either Pitot A or B. The results in Table VIII indicate then that a small error in z of about 0.0005 inch is possible when a tube is touching the surface. Any error in z should, however, rapidly decrease as the distance from the surface is increased.

22. *Velocity results.*—Explorations of total head (time-average values) were made in the boundary layer, along 12 lines normal to surface A. The first exploration was at $x = 0.0524$ C and the twelfth at $x = 0.956$ C. The wind speeds were 60 and 80 ft./sec. The incidence of the aerofoil was -0.18° . The velocity distributions were estimated from the total-head explorations (corrected as described in § 21) on the assumption that the static pressure along each normal line was constant and equal to the value measured at the surface.

The velocity coefficients (V/V_0) obtained with the Pitot tubes A and B are plotted (as dots) against (z/C), at a constant value of (x/C), in figs. 10 and 11. These points are seen to lie closely on smooth curves. The results obtained in § 10 with the small surface tubes are also plotted in figs. 10 and 11. These results are seen to lie very closely on the curves drawn through the results obtained with the Pitots A and B. The two sets of results are therefore compatible.

* Some small uncertainty in the position of the geometrical centre existed, owing to irregularities in the shape of the mouth.

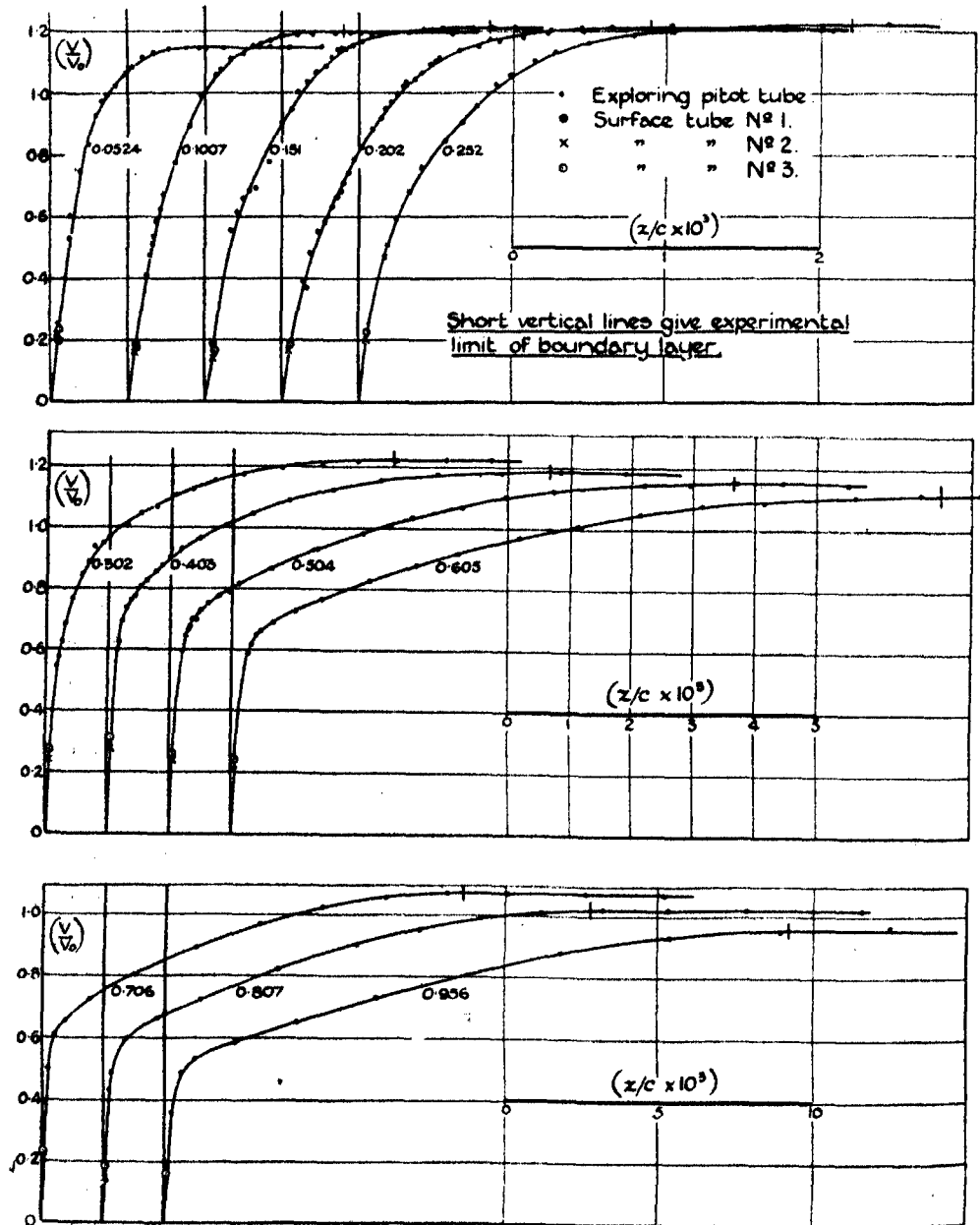


FIG. 10.—Velocity Distribution in Boundary Layer. Surface A, $\alpha = -0.18^\circ$ $V_0 = 80$ ft./sec. Values of x/c given on curves.

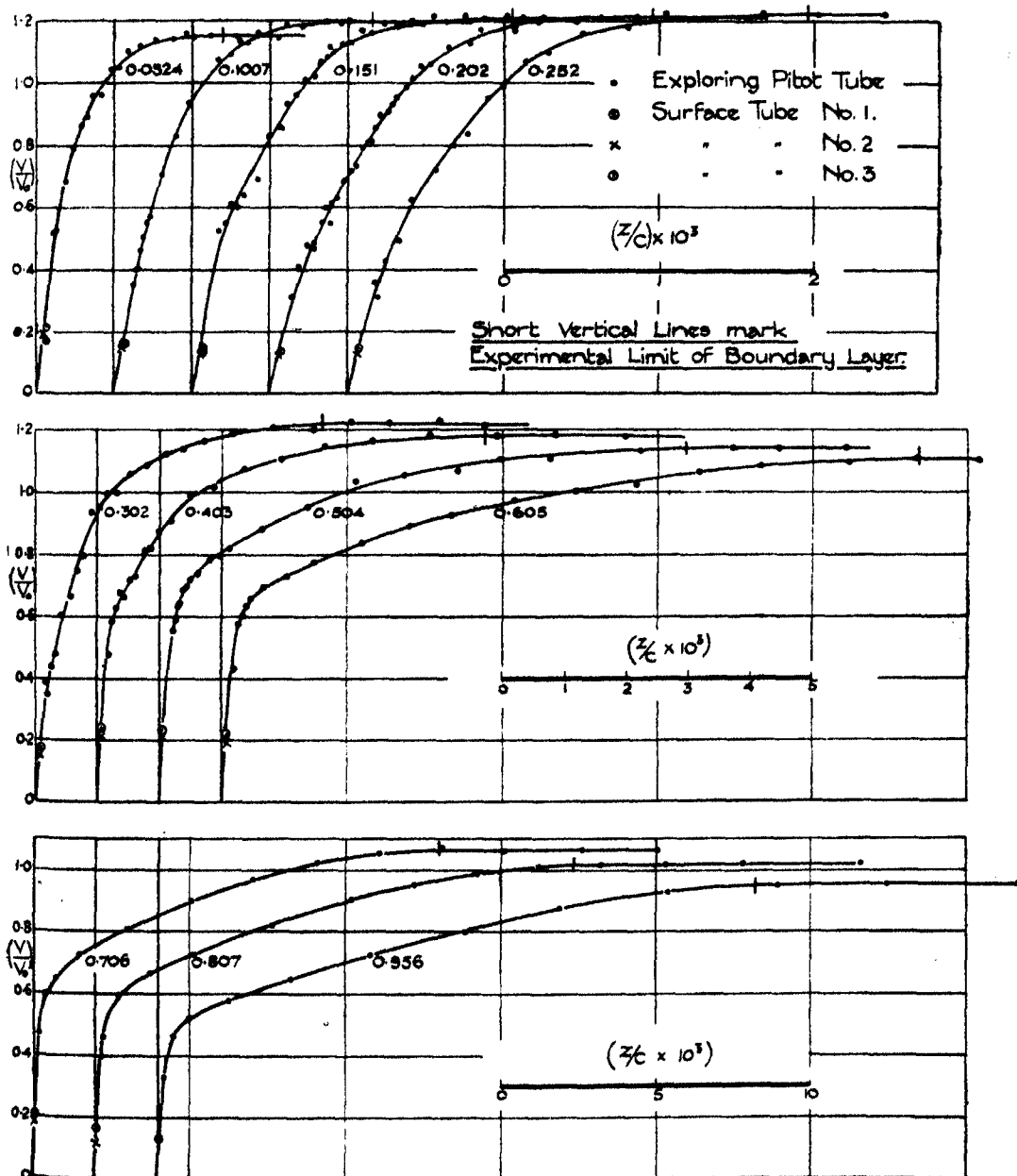


FIG. 11.—Velocity Distribution in Boundary Layer. Surface A, $\alpha = -0.18^\circ$, $V_0 = 60$ ft./sec. Values of x/C given on curves.

23. *Thickness of boundary layer.*—The total head near the surface of the aerofoil increased with the distance from the surface until eventually a constant value was reached, which was very closely the same as that in the undisturbed stream. For all practical purposes therefore the retarding influence of the surface was confined to a thin layer of air adjacent to the surface (the boundary layer). It was however difficult to estimate the thickness of this layer, because of the easy gradient of total head near the outer limit of the layer. Although it was known that some uncertainty was inevitable, an attempt was made to estimate the thickness of the boundary layer. To lessen this uncertainty the experimental observations of total head were faired. The method followed was first to plot the experimental values of total head for each section against z , and to determine the limiting value to which the curve tended. These limiting values (H_0') were found to differ very slightly from the value of the total head in the undisturbed stream (H_0). At each section the value of H_0' was taken as datum and the experimental values of $(H - H_0')$ taken just within the layer were faired, first by plotting them against z at a constant value of x , and then against x at a constant value of z . The thickness of the boundary layer (δ) at any section was obtained by extrapolation of the curve obtained when the faired values of $(H - H_0')$ were plotted against z .

24. Curves of boundary-layer thickness for the speeds 60 and 80 feet per second are given in fig. 12. At each speed, the boundary layer rapidly thickens

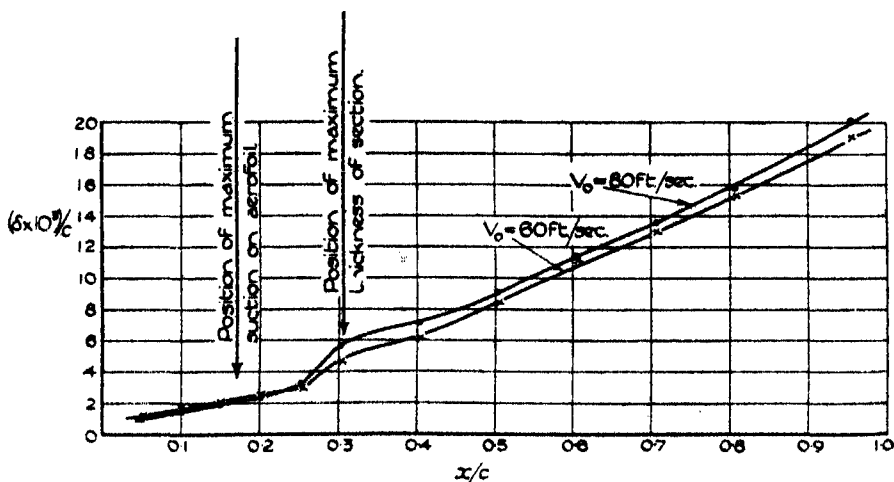


FIG. 12.—Thickness of Boundary Layer.

between the regions of maximum suction and of maximum thickness. This rapid thickening is a common feature of the flow in a boundary layer and, in

the absence of a breakaway or a sudden change of curvature of the surface, marks the region where a transition from laminar to turbulent flow takes place. It appears then that the transition ($\alpha = -0.18^\circ$) began just beyond $x = 0.25 C$ and that it was completed near $x = 0.35 C$. Some general evidence that a transition of flow occurred in this region is given in the curves of fig. 13, which have been obtained by plotting values of (V/V_0) against

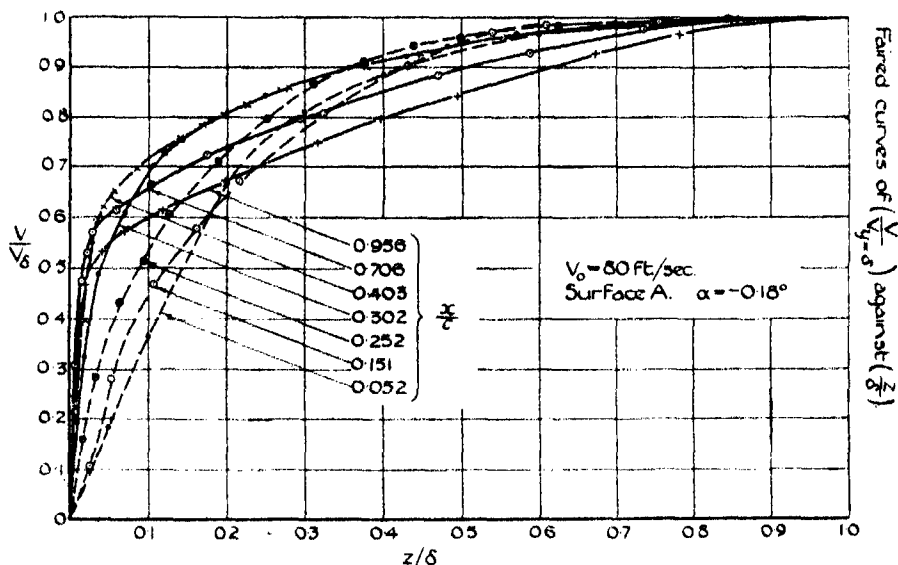


FIG. 13.

(z/δ) , at a constant value of x ($V_0 = 80$ ft. per sec.)*. Broadly speaking, these curves fall into two groups; first, those for the front part of the surface ($x < 0.25 C$), which resemble the shape associated with laminar flow, and second, those for the rear part ($x > 0.3 C$) which are typical of the shape obtained for turbulent flow. It will be noted that the curve for the first section $x = 0.052 C$ is rather odd, for it appears to have some resemblance to the curves for the turbulent flow at the rear of the aerofoil. It was probable that the flow in the boundary layer at this section was not completely laminar, for it was observed that the pressure on the surface in the immediate neighbourhood of the nose was very disturbed. As would be expected, the thickness of the boundary layer over the front part of the aerofoil was greater at $V_0 = 60$ feet per second than that at $V_0 = 80$ feet per second; and also the transition occurred later at the lower speed. It will be observed that there was no indication of any rapid thickening of the boundary layer near

* The curves for $V_0 = 60$ ft./sec. ($\alpha = -0.18^\circ$) showed similar characteristics.

the tail, such as would have occurred if the layer had separated from the surface.

25. *Estimation of the surface friction from the momentum in the boundary layer.*—The changes of momentum in the boundary layer as it flows around the aerofoil are directly related to the normal and tangential components of the pressure on its surface. The surface friction can therefore be predicted from the observations of velocity in the boundary layer, and the normal components of the pressure on the surface, which are given earlier in the paper. The form of the momentum equation used for these predictions was kindly suggested to the writers by Prof. G. I. Taylor. This equation was found to be more convenient for numerical calculation than the equation in an alternative form used by von Kármán.* For this reason it has been thought desirable to give the steps which led to the final form of Prof. Taylor's equation.

At any point p on the surface at a peripheral distance s from the nose, axes ps and pz respectively tangential and normal to the surface are taken. A consideration of the equilibrium of a rectangular element of width ds and height z (z in the first instance is taken greater than δ the thickness of the boundary layer) leads to the expression†:—

$$-f \cdot ds/\rho = \int_c (p/\rho) \cdot l \cdot d\sigma + \int_c (lu + mv) u \cdot d\sigma.$$

where f represents the intensity of surface friction, p the pressure, ρ the density, u and v the tangential and normal components of velocity, and (l, m) the direction cosines of the normal to an element $d\sigma$ of the contour of the element. The integrations are taken around the contour c . The expression is then recast into the form,

$$-f \cdot ds = \int_c (p + \frac{1}{2}\rho V^2) l \cdot d\sigma + \int_c \rho \left\{ mvu + l \left(\frac{u^2}{2} - \frac{v^2}{2} \right) \right\} d\sigma,$$

where $V^2 = u^2 + v^2$.

Neglecting v^2 and writing $v_s = -d/ds \int_0^z V dz$, the above expression becomes

$$-f = \frac{d}{ds} \int_0^z (p + \frac{1}{2}\rho V^2) dz - \rho V_s \cdot \frac{d}{ds} \int_0^z V dz + \frac{1}{2}\rho \frac{d}{ds} \int_0^z V^2 dz.$$

* 'Z. Angew. Math. Phys.,' vol. 1 (1921).

† See G. I. Taylor. 'Phil. Trans. Roy. Soc.,' A, vol. 225, p. 239.

It then follows that

$$-f = \frac{d}{ds} \int_0^z (p + \frac{1}{2} \rho V^2) dz - \rho V_s \frac{d}{ds} \int_0^z (V - V_s) dz + \frac{1}{2} \rho \frac{d}{ds} \int_0^z (V^2 - V_s^2) dz,$$

since

$$\left[-V_s \rho \frac{d}{ds} \int_0^z V_s dz + \frac{1}{2} \rho \frac{d}{ds} \int_0^z V_s^2 dz \right] = 0,$$

if the value of z be constant.

Further, the above equation also holds when z is variable and equal to δ , the thickness of the boundary layer, provided the total head H_0 outside the boundary layer be taken as the datum from which total head $(p + \frac{1}{2} \rho V^2)$ within the boundary layer is measured, since it may be assumed that $(V = V_s)$ just outside the boundary layer.

It follows therefore that

$$f = \frac{d}{ds} \int_0^\delta (H_0 - H) dz - \rho \cdot V_s \frac{d}{ds} \int_0^\delta (V_s - V) dz + \frac{1}{2} \rho \frac{d}{ds} \int_0^\delta (V_s^2 - V^2) dz.$$

Further $\frac{1}{2} \rho (V_s^2 - V^2) = (H_0 - H)$, if it be assumed that the pressure is uniform across a section of the boundary layer and the same as at the surface and therefore

$$f = 2 \frac{d}{ds} \int_0^\delta (H_0 - H) dz - \rho \cdot V_s \cdot \frac{d}{ds} \int_0^\delta (V_s - V) \cdot dz.$$

Finally, it follows that

$$\int_0^s f \cdot ds = 2 \int_0^s (H_0 - H) dz - \int_0^s V_s \cdot dM_1,$$

where

$$M_1 = \int_0^\delta \rho (V_s - V) dz.$$

26. Since the velocity values given in figs. 10 and 11 were determined from the observations taken when the total head was measured directly against the pressure at the surface, it follows from the method of derivation of the above equation for $\int_0^s f \cdot ds$, that the datum total head* must be the value measured just outside the layer. Values of $\int_0^s f \cdot ds$ calculated in this manner

from the experimental data taken at the wind speeds 60 and 80 ft./sec. are plotted against s in fig. 14. The values obtained from the integral of the

* The datum total head measured just outside the layer occasionally differed very slightly from the total head in the undisturbed stream.

frictional intensities given in Table II are also plotted in this figure. The curves drawn through the two series of points are seen to lie fairly close

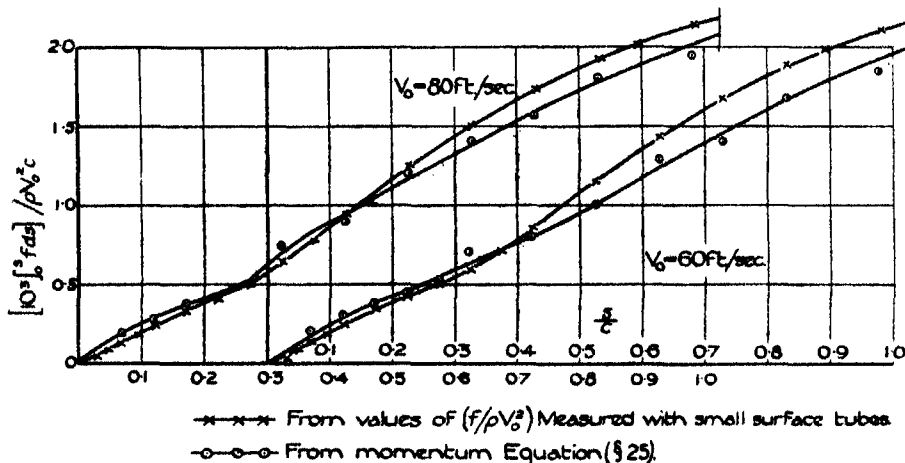


FIG. 14.

together, except near the nose, at sections $s = 0.068 C$ and $0.120 C$. That there were differences at these sections is not surprising, for the value of $\int_0^s V_s dM_1$ for the section $s = 0.068 C$ had to be obtained by extrapolation, for no measurements of velocity were made in the boundary layer forward of this section. Also it is not certain that the condition assumed in the derivation of the momentum expression, namely, that the static pressure at all points in a section of the boundary layer is uniform and the same as that at the surface, holds with sufficient accuracy at the nose, since the curvature of the surface is rapidly changing in this region. It is of interest to mention here that observations taken in the section $x = 0.956 C$ at the tail showed that the static pressure within the boundary layer was constant and the same as that at the surface.

27. It is shown in § 13 that at $\alpha = -0.18^\circ$ the drag of the aerofoil obtained from the intensities of surface friction was only 2 per cent. smaller than the sum of the values of $\int_0^s f \cdot ds$ for the two surfaces. The values of $\int_0^s f \cdot ds$ for the surface A obtained from the momentum equation of § 25 were $0.00209 \rho CV_0^2$ (80 ft./sec.) and $0.00200 \rho CV_0^2$ (60 ft./sec.). Since at $\alpha = -0.18^\circ$ the value of $\int_0^s f \cdot ds$ for surface B can be taken as the same as that for Surface A, the values of K_D (frictional) are 0.00410 (80 feet per second) and 0.00390 (60

feet per second). These values of K_D are compared in Table IX with those obtained in § (13) from the frictional intensities measured with the small surface tubes and those obtained in § (18) from the measurements of the total and form drags. The three series of results are seen to be in reasonably close agreement. In general, then, the accuracy of the experimental work described in the paper is satisfactory.

Table IX.—Values of K_D (frictional). $\alpha = -0.18^\circ$.

Source of Results.	$V_0 = 60$ ft./sec.	$V_0 = 80$ ft./sec.
From observations taken with the small surface tubes. § (13)	0.00425	0.00435
From measurements of total drag and form drag § (18)	0.00395	0.00395
From observations of velocity in boundary layer. (Momentum Equation.) § (25)	0.00390	0.00410

28. *Details of aerofoil section.*—The section was derived from a circle by a conformal transformation of the generalised Joukowski type given by the expression $(\zeta - nc)/(\zeta + nc) = (z - c)^n/(z + c)^n$. An outline of the method of calculating the shape is given in the paper referred to earlier in § (15). The values of the shape parameters were $(a/c) = 1.10$ and $n = 1.95$. This theoretical section had a tail which tapered gradually to a sharp edge; and since this was a shape which could not be reproduced with great accuracy on the model, a small part of the tail was cut off and the shape completed by rounding off the trailing edge. The chord length of the theoretical shape was 40.52 inches, and that of the section used in the experiments 39.7 inches. The maximum thickness was 5.98 inches and occurred at one-third of the chord.

As mentioned earlier in § 2, the central part of the aerofoil of span 6 inches was cut from a hollow gunmetal casting. The shape of surface A of the finished model was checked on a milling machine before the experiments were commenced. It was found that the shape from the nose to the maximum ordinate agreed, within the accuracy of measurement, with the theoretical shape, but that there was a small difference from the theoretical shape over the region $x = 18$ inches to 27 inches. The maximum difference occurred at about $x = 22.5$ inches, and was such that the actual value of y was about 0.996 of its theoretical value. Only the contours for the theoretical shape have been given in the paper (Table V), for it is unlikely that the small departure of the

actual shape from the theoretical shape, which occurs just beyond the maximum thickness, will effect to any measurable extent the flow around the surface.

29. *Summary.*—The intensity of friction over the surface of a large symmetrical aerofoil of the Joukowski type (chord 39.7 inches) has been determined from measurements of velocity taken very near the surface with small surface tubes of the Stanton type. The characteristic feature of this type of tube is that the inner wall of the tube is formed by the surface itself. Three tubes with openings 0.0020, 0.0032 and 0.0044 inch respectively were used. These tubes allowed measurements of velocity to be taken at distances of 0.002 to 0.003 inch from the surface.

The velocity gradients at the surface $(\partial V/\partial z)_{z=0}$ were determined from these velocity measurements, and the intensities of the surface friction (f) from the well-known relation $f = \mu (\partial V/\partial z)_{z=0}$.

The results obtained showed that on each surface the frictional intensity had a maximum value at a short distance from the nose, and a second and larger maximum value just beyond the first. As the incidence was increased (0° to 6°), the maximum values on the upper surface increased and moved nearer the nose, whereas those on the lower surface decreased slightly and moved towards the tail. The first maximum value was associated with laminar flow, and the second with turbulent flow in the boundary layer.

Measurements of velocity in the boundary layer were also made with small exploring tubes, and these measurements were found to be compatible with those made nearer the surface with the surface tubes.

Evidence on the general accuracy of the values of the frictional intensity was obtained from a comparison of the frictional drag of the aerofoil estimated from them with values obtained by two other methods. In the first method, the frictional drag was determined by subtracting the form drag, obtained from the normal pressures on the surface, from the total drag estimated from the total-head losses in the wake; and in the second, the frictional drag was estimated from an equation derived from a consideration of the momentum and pressure changes in the boundary layer. The values of the frictional drag obtained by the three different methods were found to be in reasonably close agreement.

30. In conclusion, the authors wish to express their great indebtedness to Messrs. J. H. Warsap and C. Scruton, who assisted in the experimental work; to Mr. A. Monk, who made the metal aerofoil and the exploring Pitot tubes; and to Mr. J. Barber, who successfully overcame the great difficulties involved in the construction of the small surface tubes.

*Observations of the Amount of Ozone in the Earth's Atmosphere,
and its Relation to other Geophysical Conditions.—Part IV.*

By G. M. B. DOBSON, D.Sc., F.R.S.

With Reports by Dr. H. H. KIMBALL and Dr. E. KIDSON.

(Received July 14, 1930.)

In the previously published papers* on this subject it has been shown that there is a marked relation between the amount of ozone in the upper atmosphere and the type of atmospheric pressure distribution. By means of simultaneous observations at six stations in N.W. Europe, a fair idea of the distribution of ozone with different pressure distributions was obtained. To get further insight into this relation it was necessary to know the distribution of ozone over the world at different times of the year. The instruments were, therefore, redistributed to get observations in widely different latitudes, and a year's observations have been taken at these stations. While the results for one year only cannot establish the annual variations with great accuracy, they are enough to show the main features, and several years' observations would be necessary to give a greatly improved accuracy.

The places where the observations have been made are as follows :—

Place.	Latitude.	Longitude.
Arosa (Switzerland)	46° 45' N.	9° 40' E.
Table Mountain (California)	34° 22' N.	117° 41' W.
Helwan (Egypt)	29° 50' N.	31° 10' E.
Kodaikanal (India)	10° 10' N.	77° 30' E.
Christchurch (New Zealand)	43° 30' S.	172° 40' E.

An instrument was lent to Prof. Pontremoli to go with the Italian Airship Expedition to the Arctic in order to get observations in very high latitudes. Unfortunately, owing to the disaster to the airship, in which Prof. Pontremoli was killed, no results were obtained. During the summer of 1929 Dr. Götz (who has most kindly made observations for us at Arosa, extending continuously over three years) went himself to Spitzbergen, taking one of our instruments with him. When the other instruments were redistributed, the Arosa

* 'Proc. Roy. Soc.,' A, vol. 110, p. 660 (1926); vol. 114, p. 521 (1927); and vol. 122, p. 456 (1929).

Table I.—Daily Ozone Values.

Arosa.

Day.	1928.		1929.					
	Nov.	Dec.	Jan.	Feb.	March.	April.	May.	June.
1	—	—	—	274	313	312	329	—
2	—	—	—	299	307	371	325	277
3	—	—	285	288	315	352	—	282
4	—	245	295	253	315	358	314	—
5	224	233	322	—	283	378	295	300
6	235	234	296	285	—	419	290	—
7	226	239	—	302	292	—	285	275
8	237	257	267	328	265	328	285	—
9	—	262	292	322	280	330	—	274
10	—	262	288	330	—	350	—	—
11	219	273	267	364	276	361	—	261
12	—	—	258	338	—	351	—	—
13	193	—	226	363	246	370	—	—
14	195	281	—	378	—	335	—	—
15	197	266	262	338	250	—	—	—
16	—	240	—	314	250	—	—	—
17	235	228	—	340	277	328	—	—
18	255	—	302	—	299	308*	—	—
19	239	—	—	370	303	287	—	—
20	240	237	259	374	300	272	330	—
21	223	254	252	317	278	280	302	—
22	225	238	—	306	—	—	295	—
23	205	252	261*	287	—	315	294	—
24	—	248	—	292	—	—	282	—
25	—	237	—	326	—	333	282	—
26	—	259	—	—	293	327	264	—
27	240	—	305	310	282	333	281	—
28	—	245	327	350	—	312	289	—
29	—	—	297	—	271	345	293	—
30	252	237	300	—	283	325	285	—
31	—	318	265	—	303	—	—	—
Means	226	252	281	322	285½	335	296	(278)

* Ozone value falling.

instrument was still left there in order to get a long series of observations, as this proved to be an excellent situation. As in the previous observations, the exposed plates were all returned to Oxford and were standardised, developed and measured here.

Table I gives all the results for the four new stations and also those for Arosa which have been obtained since the publication of the last paper. Figs. 1A and 1B give the annual variations for all the stations where we have had observations. These are arranged in order of latitude. Unfortunately with

Table I.—Daily Ozone Values—(continued).

California.

Day.	1928.					1929.							
	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	March.	April.	May.	June.	July.	Aug.
1	224	218	219	180	221	252	—	272	263	256	269	232	222
2	220	215	205	184	—	—	268	257	260	242	260	223	220
3	218	214	228	197	226	238	260	265	263	245	—	224	236
4	220	220	216	197	233	236	241	246	—	256	—	224	234
5	215	220	213	191	—	262	253	255	270	271	252	228	237
6	220	218	216	202	208	—	—	—	305	269	261	227	225
7	208	212	217	216	198	275	276	281	310	269	276	238	225†
8	213	209	215	207	198	230	—	268	298†	253	—	240†	224
9	220	203	212	195†	214	222	242	251	284	252	272	226	235
10	222	220	208	195	218	233	245	—	291	202†	265	226	232
11	227	212	—	184	217	228	—	288	252	257	255	220	232
12	228	213	274	198	225	220	278	286	306	250	261	240	232
13	226	218	270	232	260	211	278	—	300	251	227	230	227
14	232	214	233	240	292	224	310	273	281	—	231	226	248
15	219	203	215	245	300	—	278	286	272	255	238	237	239
16	218	205	206	218	249	—	284	288†	273	262	245	238	234
17	215	204	220	222	244	251	—	268	260	239	235	228	236
18	221	206	226	204	253	210	—	279	260	245	223*	226	225
19	222	204	218	231	243	—	295	—	253	282	224	230	228
20	226	208	230	236	240	—	259	262	265	280	219	242	—
21	225	201	210	225	230	297	227	—	283	282	225	243	230
22	225	195	202	220	248	275	242	245	283	—	230	240	233
23	216	200	198	197	230	294	262	298	308	266	217	240	217
24	220	200	202	—	220	257	264	342	258†	252	225	240	—
25	215	209	199	214	212	255	242	305	290	244	212	238	—
26	220	204	194	215	204	264	296	283	288	262	221	241	—
27	216	217	202	210	205	—	264	255	305	327	220	235	—
28	220	218	205	222	218	—	276	240	273	268	239	234	—
29	212	205	186	223	225	235	—	227	269	260†	237	—	—
30	222*	205	210	196	228	—	—	265	262	280	232	229	—
31	219	—	191	—	238	—	—	275	—	253	—	230	—
Means	220	210	215	210	231	246	265	272	279	261	240	232†	(230‡)

* Ozone value rising. † Ozone value falling. ‡ Falling a.m., rising p.m.

the instruments used up to now it has not been possible to get observations in the higher latitudes during the winter, owing to the low altitude of the sun even at noon and the prevalence of cloud. The results given, however, leave no doubt about the general distribution and annual variations over the greater part of the earth. In order to show the distribution with latitude at different times of the year, the same results are presented in a different manner in figs. 2A and 2B, which also include the valuable results obtained by Dr. Götz at Spitzbergen during the summer of 1929.

Table I.—Daily Ozone Values—(continued).
South India.

Day.	1928.				1929.							
	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	March. [†]	April. [†]	May. [†]	June.	July.	Aug.
1	—	205	—	—	188	192	195	—	207	—	—	213
2	—	—	198	—	194	—	203	—	—	—	201	—
3	—	195	207	—	193	—	192	—	—	—	201	211
4	—	—	—	—	193	197	200	—	—	—	210	—
5	—	206	187	—	197	179	194	210	200	—	—	179
6	—	200	—	203	190	184	197	204	—	—	—	182
7	—	202	—	—	—	—	190	190	—	—	—	190
8	—	203	—	—	—	193	195	188	—	—	—	194
9	—	208	—	—	—	196	184	—	203	—	—	202
10	—	207	—	198	180	188	197	—	209	—	212	205
11	—	—	—	—	197	184	—	—	—	—	—	—
12	205	—	—	—	198	196	192	209	—	—	—	215
13	205	—	—	—	197	196	196	217	215	217	211	209
14	213	—	—	—	202	195	199	—	217	216	—	212
15	217	213	190	186	203	188	—	206	228	—	220	206
16	210	—	—	—	198	191	197	208	206	212	—	212
17	209	—	—	—	202	—	212	205	212	—	—	—
18	209	—	—	174	192	191	—	206	215	—	206	—
19	202	—	195	203	195	191	208	203	210	—	—	204
20	209	—	—	194	188	196	—	205	217	—	212	—
21	195	—	—	186?	187	200	—	195	214	—	—	—
22	—	—	—	188*	193	195	199	—	193	205	222	—
23	—	—	—	190	180	203	—	—	212	198	222	—
24	210	—	—	174	192	195	—	—	217	210	—	—
25	203	195	198	—	—	202	213	—	205	—	209	—
26	203	—	—	—	190	207	210	—	212	—	211	207
27	202	—	—	—	182	200	200	206	—	207	211	214
28	205	—	179	—	186	200	199	—	—	—	—	210
29	204	192	—	—	—	—	202	—	—	—	—	—
30	202	204	—	175	—	—	—	202	—	—	—	214
31	—	—	—	195	—	—	195	—	—	—	207	220
Means	206	202½	193	189	192	194	199	204	211	209	211	205

* Ozone value falling.

† Dates from March 2 to May 27 are doubtful by one day.

The low and uniform value of the ozone content throughout the autumn hemisphere is noteworthy and is of great importance in connection with the theory of the variation of ozone with pressure conditions. It is also of interest to see that the ozone value in India seems to be unaffected by the setting in of the monsoon, so that its behaviour in this respect differs entirely from that associated with cyclones and anticyclones in temperate regions. The general results are so clearly seen in figs. 1 and 2 that no further discussion of them is necessary.

Table I.—Daily Ozone Values—(continued).

Egypt.

Day.	1928.				1929.									
	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	March.	April.	May.	June.	July.	Aug.	Sept.	Oct.
1	—	—	214	196	212	—	—	—	206	No Photographs.	—	—	229	205
2	—	—	—	—	212	—	231	245	268		—	—	235	222
3	—	—	198	195	227	—	242	240	—		—	231	241	233
4	—	—	203	190	—	—	—	228	—		—	—	—	—
5	—	—	206	195	218	226	266	—	—		—	—	238	212
6	—	—	211	204	258	212	—	—	—		—	245	237	212
7	—	—	206	—	244	218	—	223	—		—	—	230	—
8	—	—	—	—	230	224	—	238	—		—	230	230	208
9	—	—	—	221	230	—	—	—	—		—	—	236	—
10	—	—	—	222	—	226	263	254	—		—	237	231	—
11	—	—	193	218	—	230	—	—	—	No Photographs.	—	235	230	—
12	—	—	203	213	—	236	—	266	—		—	235	231	—
13	—	—	—	—	246	226	—	259	—		—	233	—	—
14	—	—	195	—	253	240	—	252	—		—	—	247	—
15	—	—	—	215	260	245	—	266	—		—	234	235	—
16	—	—	—	210	265	253	275	252	—		—	—	233	—
17	—	—	—	—	235	228	254	258	—		—	—	—	—
18	—	—	—	199	202	260	250	247	—		—	221	224	—
19	—	—	—	207	210	—	266	—	—		—	229	230	—
20	—	205	—	—	220	—	251	—	—		—	227	222	—
21	—	206	—	215	—	266	243	—	—	No Photographs.	—	234	—	—
22	209	222	222	225	238	—	246	—	—		—	—	233	—
23	223	245	—	235	236	—	—	239	—		232	227	232	—
24	—	221	206	218	242	—	—	239	—		220	230	223	—
25	—	—	217	—	—	266	258	260	—		221	225	—	—
26	210	215	200	203	245	231	254	—	—		230	233	230	—
27	—	202	216	203	—	245	232	—	—		237	222	—	—
28	—	202	206	—	221	233	226	—	—		234	228	—	—
29	—	—	210	210	232	—	—	—	—		—	229	223	—
30	—	212	—	226	232	—	—	215	—		238	234	229	—
31	—	—	—	215	—	—	—	—	—		230	—	—	—
Means	—	(214)	207	211	233	237	250	246	—	—	(230)	231	232	(215)

Connection between Ozone Content and Pressure Conditions in different parts of the World.

For the proper study of the connection between the amount of ozone and the meteorological conditions, a number of observing stations are necessary, but it is of interest to know whether the general connection found in N.W. Europe holds also in other parts of the world. Both in Chile and S. India the meteorological conditions are very constant and no important variations of either ozone or pressure occurred during the series of observations. In

Table I.—Daily Ozone Values—(continued).
New Zealand.

Day.	1928.					1929.										
	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	March.	April.	May.	June.	July.	Aug.	Sept.	Oct.	Nov.
1	—	—	—	—	—	—	262?	—	—	258	—	296	349	—	317	251
2	—	—	305	—	—	—	251	—	—	273	—	290	354	286	312	—
3	—	346	298	—	298	—	262	—	—	247	—	296	342	344	—	—
4	—	333	298	—	282†	—	246	—	—	266	—	319	—	328	310	—
5	—	321	342	—	290	—	260	216	—	—	—	—	—	347	291	268
6	355	—	—	284*	264	245	258	—	—	—	—	—	343	351	—	287
7	329	—	322	270	261	—	—	—	—	263	—	—	311	—	318	302*
8	328	—	296	270	—	270	—	239	216	252	—	—	281†	—	339	—
9	—	—	324†	255	—	272	255	—	225	281	—	—	—	332*	324	282
10	286	337	327	—	—	—	242	—	—	—	—	—	—	363	309	—
11	—	326	346†	308	—	252	240*	236	—	—	—	305	—	330	317	—
12	—	—	318	319†	—	224	253	243†	—	—	337	292	—	273	316	286
13	—	340	350	250	—	—	—	221	—	—	335	—	—	280	—	282
14	—	—	355	264*	282	—	233	212	—	—	—	—	288	297	326	—
15	—	—	341†	—	—	248	241	—	240	—	—	—	—	—	306	288
16	—	338	314	271	—	—	230	—	—	258	—	—	302	325	—	305
17	—	370	297	276	246	—	260	—	270	253	—	—	326	309*	—	—
18	—	—	—	252	—	227	236	231	250*	—	—	—	—	—	295	—
19	—	338	338	252*	—	—	256	—	258	252	—	303	328	295	—	—
20	—	345	330	263	—	—	230	—	—	250	—	321	—	—	—	—
21	—	—	—	270	—	—	219*	—	—	247	—	—	—	316†	307	256
22	318	—	—	285†	—	—	232	231	245	260	262	345	—	—	—	265
23	—	325†	296	276	—	—	—	222	236	268	—	341	340	305	—	270
24	—	353	—	—	—	—	225	—	252	—	319	—	351	322	—	—
25	—	391	—	—	—	—	220	228	—	—	346	—	—	322	312	—
26	—	350	—	298	—	272	236	217†	—	—	—	—	305	330	—	—
27	—	360	—	—	—	259	237	—	—	281	298	—	325	346	—	—
28	—	358	—	301	—	—	235	—	—	285	—	—	285	330	—	—
29	—	309	309*	293	257	250	—	—	270†	280	320	—	321*	—	286	—
30	—	—	—	—	257	245	—	—	—	270	—	318	320	293	—	—
31	—	—	—	—	—	240	—	—	—	275	—	325	326	—	269†	—
Means	(323)	344	322	277	(271)	250	242	227	(246)	264	(317)	313	322	319	309	278†

* Ozone value rising.

† Ozone value falling.

‡ Falling a.m., rising p.m.

California no intense cyclones passed near the observing station during the time observations were in progress, but all large increases in the amount of ozone occurred with N.W. winds in the troposphere (see p. 420). In Egypt and New Zealand, however, there is fairly clear evidence of the same relationship as in Europe. Since the daily weather maps are not published for New Zealand, and also since it was most desirable that the study of this matter should be made by someone having an intimate knowledge of the meteoro-

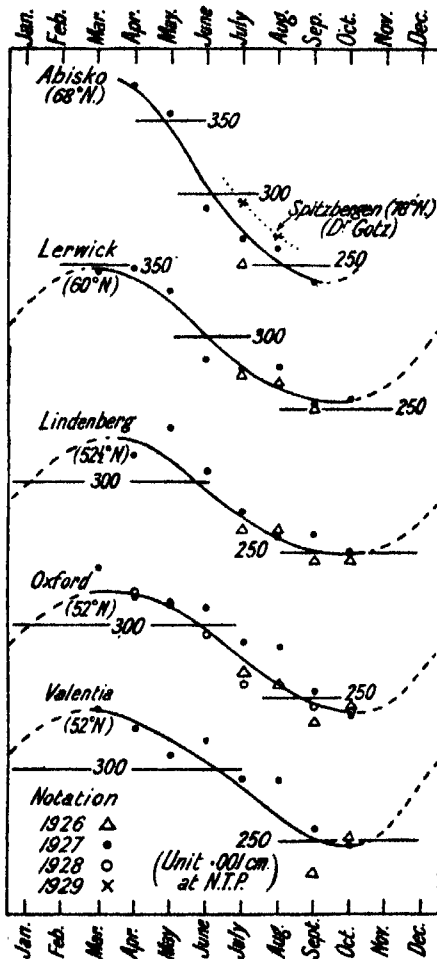


FIG. 1A.

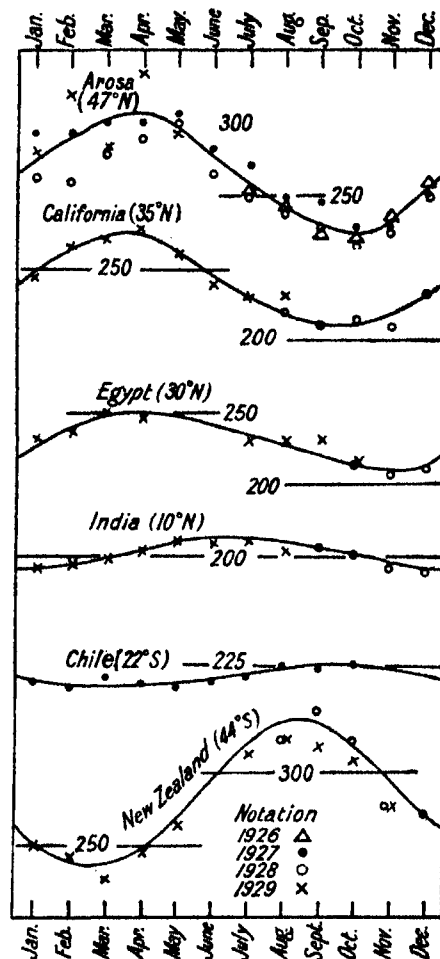


FIG. 1B.

logical conditions in each region, it was arranged that Dr. Kimball of the Weather Bureau, Washington, and Dr. Kidson, Government Meteorologist in New Zealand, should examine the subject in their respective areas. They both have most kindly supplied reports of their work which are given *verbatim* overleaf.

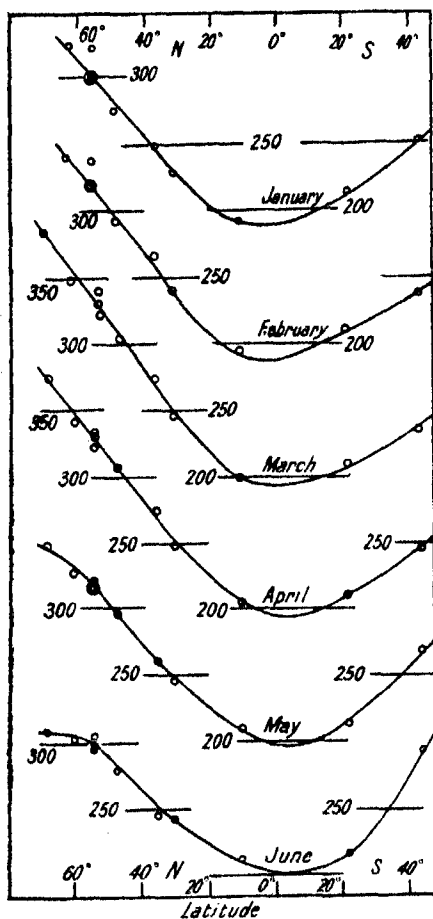


FIG. 2A.

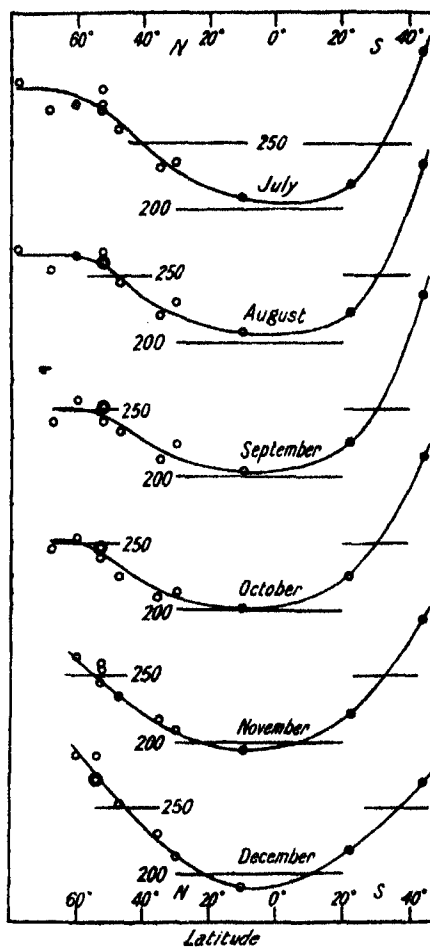


FIG. 2B.

APPENDIX 1.

The Relation of Variations in the Ozone Values obtained at Table Mountain, California, to the Meteorological Conditions.

By HERBERT H. KIMBALL, U.S. Weather Bureau.

"This study has been made at the request of Dr. Dobson, since certain relations found to exist in Europe apparently do not hold in Southern California.

There is available for this study the following material:—

(1) Ozone values based on measurements by Dobson of photographs made at Table Mountain of the sun's spectra in the ultra-violet, and kindly forwarded to me.

(2) 8 a.m. and 8 p.m. (5 a.m. and 5 p.m., 120th meridian time), daily weather maps of the Northern Hemisphere made up by the U.S. Weather Bureau forecasters.

(3) Pilot balloon observations made twice daily at Los Angeles and Oakland (California), Reno (Nevada), and Modena (Utah); but since the three last-named stations are at a considerable distance from Table Mountain, with mountain ranges intervening, the wind direction and velocity data obtained by them have been given little weight. Wind directions for Table Mountain have therefore been obtained principally from the Northern Hemisphere Daily Weather Maps and the Los Angeles pilot balloon observations. The co-ordinates of these two stations are as follows: Los Angeles, latitude $34^{\circ} 3' N.$, longitude $118^{\circ} 15' W.$, altitude 330 feet (101 metres); Table Mountain, latitude $34^{\circ} 22' N.$, longitude $117^{\circ} 41' W.$, altitude 7500 feet (2286 metres).

Certain peculiarities of meteorological conditions in Southern California should be noted, as follows :—

1. In summer there is a permanent low pressure area central at about Yuma, Arizona, with a trough extending northwards over the Valley of California to Sacramento or beyond.

2. In winter there is a permanent high pressure area over the Rocky Mountain plateau, often central in Idaho. It is not always clear from the weather map whether this High is real, or is the product of faulty reduction of pressure readings to sea level. In any event, the wind, and especially cloud movements, do not always appear to be under its control.

3. During the period covered by this note, August 1, 1928, to May 10, 1929,* not a single high pressure or low pressure area was central over southern California.

4. The proximity of the cool waters of the Pacific Ocean on the west border of California is a factor in determining surface wind direction, and gives it a decided diurnal variation.

5. The North Pacific High approaches the coast of North America in summer, and occasionally an offshoot from this High enters the United States north of California.

6. In winter, offshoots from the North Pacific Low enter the United States, usually over the state of Washington. As they move east it frequently happens that a secondary Low forms as far south as Colorado or Arizona. It

* Summer observations were not included as there were only very slight variations of either ozone or pressure.—G.M.B.D.

thus occurs that Table Mountain is in the outer edges of Highs and Lows, but never at their centres.

An examination of the ozone values shows that during August and September the daily departures from the monthly means exceed Dobson's* estimate of the probable error of a single determination (0.005 cm., $= \pm 2.3$ per cent. in August and ± 2.4 per cent. in September) less than half the time. There is, however, a systematic change from a period of plus departures to a period of minus departures that is evidence against the variations in the measurements being entirely fortuitous.

From October to April, inclusive, the departures, and especially those with the plus sign, show an increase in magnitude. The high plus departures are usually associated with a flow of cold air at the surface from the front of an area of high pressure towards the rear of an area of low pressure. This was the case on October 12-13, November 13-16, December 13-15, January 21-23, February 26, March 13 and 24, and April 23 and 27. On February 14 and 19, while there was a surface air current from the front of a High toward the rear of a Low, it was not accompanied by a fall in temperature. On all the above dates pilot balloon observations have shown that the wind to the height reached by the balloons, often about 10,000 metres, was from some point between west and north.

Minus ozone departures do not appear to have been associated with any special type of meteorological conditions.

Omitting from consideration the ozone data for August, September and May, when surface pressure conditions in Southern California are dominated almost continuously by the Pacific High and the Yuma Low, if the daily percentage departures are plotted on idealised High and Low pressure charts, such as have been prepared by Dobson† they will appear on the lower side of the High and on the rear of the Low. While the signs of the departures are nowhere consistently the same, their average values when expressed as a percentage of the monthly mean values are about $+2$ per cent. on the rear of the Low, $+1$ per cent. on the front lower quadrant of the High, and -3 per cent. on its rear lower quadrant. The low value of these average departures is no doubt due to the fact that on only a few occasions are the meteorological conditions in Southern California dominated by well-marked high or low-pressure areas."

* 'Proc. Roy. Soc.,' A, vol. 110, p. 680 (1926).

† 'Proc. Roy. Soc.,' A, vol. 122, p. 456.

APPENDIX 2.

The Relation between Weather and the Amount of Ozone in the Earth's Atmosphere above Christchurch, New Zealand.

By E. KIDSON, O.B.E., D.Sc., F.Inst.P.

"1. *Introduction.*—In this paper are discussed 13 months' observations of the amount of ozone in the atmosphere at Christchurch, New Zealand. The method used is that of Dr. G. M. B. Dobson* and the spectroscope was provided by him. The observations were made by Dr. C. Coleridge Farr, F.R.S., Professor of Physics at Canterbury College, Christchurch, or members of his staff. The plates were returned to England after exposure and measured under Dr. Dobson's supervision.

2. *Annual Variation.*—One year's observations are clearly very slender material from which to derive a reliable annual variation, but the results are very definite and in good agreement with those obtained elsewhere. Consequently, there can be little doubt as to the accuracy of the general features indicated by them. The monthly means have been plotted in fig. 3, in which the values for the two Augusts have been combined to form a single mean. The curve suggests that the normal variation would be approximately of sine curve form with the maximum in September and the minimum in March, and

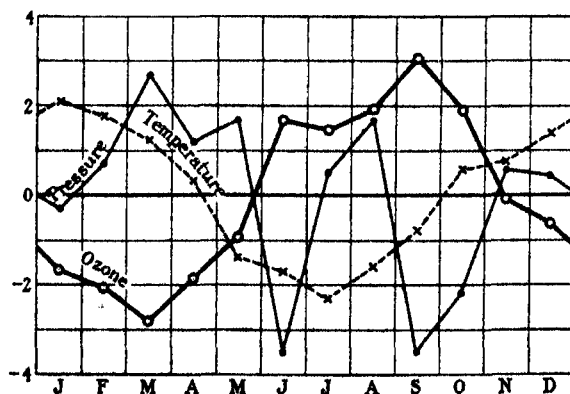


FIG. 3.—Variation of Ozone, Pressure and Temperature, August, 1928, to August, 1929. (1 scale div. = 0.02 cm. O₃, 0.1 inch, or 5° F.)

an amplitude of about 0.1 cm. Ozone values are decreasing while the sun shines on the South Pole and increasing while the South Pole is in darkness.

* Dobson, Harrison and Lawrence, 'Proc. Roy. Soc.,' A, vol. 110, p. 660 (1926); vol. 114, p. 521 (1927); and vol. 122, p. 456 (1929).

Monthly means of pressure and temperature derived from the days on which the ozone was measured are also plotted in fig. 3. The pressure values are obtained from readings at 9 a.m. and the temperatures from the means of the daily maximum and minimum. Both pressure and temperature curves would be very similar if the means were derived from all days in each month. Since the normal annual variations of surface pressure and temperature differ widely from what is described above as the probable variation of ozone, one would not expect any close relationship, either direct or inverse, between the curves. Actually, there appears to be no connection between those for surface temperature and ozone. There is, however, a strong suggestion that some of the irregularities in the ozone curve are associated with variations of pressure, ozone values tending to be low when the pressure is high. Possibly this is due to a more vigorous circulation when pressures are low.

3. *Correlation with Pressure and Temperature.*—A cursory inspection does not reveal any close connection between the daily ozone values and pressure. In order to correlate the two quantities it is necessary to eliminate, as far as possible, the annual variation. The method adopted by Dobson is to use departures from the mean of all the observations in each month. Owing to the great magnitude of the annual variation, this method, especially in some months, is a very rough one. At the present stage, however, it appears to be the only one available. Unfortunately, in order that a determination of the amount of ozone may be made, it is necessary that the sun should shine in the midday hours. Consequently, as will be seen from Table I, in some months the number of observations is very small. Furthermore, the observations are not evenly distributed amongst the various types of weather. The finest weather in Christchurch is associated with south-westerly winds and rising pressure and there is naturally a preponderance of ozone observations taken under these conditions.

The correlation between the departures from the monthly means of ozone amount and pressure respectively was, then, determined. The coefficient obtained was -0.19 from 173 days' observations. Though evidently real, this value is very small, much smaller than that found by Dobson in England. There were indications that a closer correlation would be obtained with the pressure of the day preceding the ozone observation, rather than with that of the actual day. This proved to be the case, a coefficient of -0.32 being obtained. For the pressure of two days before it was -0.26 .

In order to see if there was any annual variation in the relation with pressure, the daily departures from the mean were correlated separately for each month.

The results are given in Table II. Owing to the small number of observations, especially in some months, it is obvious that little reliance can be placed on the individual values. They do indicate, however, that the correlation is closer in the winter than the summer half-year, and when the ozone values are high than when they are low. Table II also gives the corresponding values for the pressure of one and two days previous, respectively. In these the seasonal variation seems to disappear, a result which is somewhat surprising.

Table II.—Monthly Correlations of Ozone Amount and Pressure.

Month.	Number of observations	Correlation with pressure.		
		Same day.	Day before.	2 days before.
January	12	-0.05	+0.03	-0.33
February	24	-0.18	-0.38	-0.16
March	11	+0.37	-0.42	-0.72
April	10	-0.12	+0.04	-0.31
May	19	-0.02	-0.22	-0.28
June	7	-0.19	-0.85	+0.12
July	12	-0.19	+0.10	-0.01
August	14	-0.54	-0.56	-0.46
September	17	-0.62	-0.65	-0.42
October	19	+0.02	-0.35	-0.26
November	19	-0.01	-0.22	-0.40
December	9	-0.04	-0.43	-0.57
Year	---	-0.19	-0.32	-0.26

The correlation between ozone amount and temperature determined in the same way as that for pressure, is found to be -0.26.

4. *Relation to Weather.*—From a study of all the material at his disposal, Dobson and his co-workers (*loc. cit.**) arrived at certain tentative conclusions regarding the occurrence of ozone in the atmosphere. These may be described briefly as follows :—

The layer of maximum density is situated at a height of about 50 km. above the surface of the earth. The ozone is produced principally by some agency the nature of which is not fully understood, but which can act in darkness as well, at any rate, as in daylight. Solar radiation tends on the whole to reduce the amount of ozone.

As a consequence of the foregoing, ozone is most abundant in the polar regions in spring. In the autumn the difference between polar and equatorial

* *Loc. cit.* Dobson, Harrison and Lawrence. Götz and Dobson, 'Proc. Roy. Soc.,' A, vol. 125, p. 292 (1929).

regions is very much reduced. There is a large annual variation in high latitudes with a maximum in spring and a minimum in autumn. At the equator the annual variation disappears and values are uniformly low.

According to these ideas, with which the Christchurch observations are in agreement, the amount of ozone in temperate latitudes will increase, especially in winter and spring, if currents at very high levels in the atmosphere tend to transport air from higher latitudes. Equatorial currents, on the other hand, will cause a reduction.

Dobson (*loc. cit.*) has determined the average distribution of ozone in the cyclone and the anticyclone in north-western Europe. Cyclones are not normally of frequent occurrence in the New Zealand area. During the year with which we are now concerned, they were unusually numerous but, owing to the presence of cloud, observations when the centres were near Christchurch are few. In any case it is clear that it would be quite impossible to determine the average distribution over any type of pressure system from one year's observations at a single station. The moving anticyclones of the Southern Hemisphere with their intervening low-pressure troughs are, however, a well-known feature of the general circulation. The low-pressure troughs, especially in high latitudes, are frequently very complicated, but the anticyclone centres and the high-pressure ridges extending from them in a north and south or north-west and south-east direction, are usually fairly clearly marked. The writer has had access to all the available weather charts of the Australian and New Zealand regions and has gradually reached the conclusion* that the anticyclones and low-pressure troughs are due to a series of very regular waves at very high levels in the atmosphere. Of these there are probably eight in the circuit of the globe. Most of the irregularities in the surface manifestations of these waves seem to be due to effects in the lower air layers. It seemed likely, therefore, that the most profitable line of investigation would be to attempt to relate the ozone values with these pressure waves. This was done by determining as nearly as possible the distance of Christchurch in degrees of longitude on each observation day from the nearest wave crest, the measurement being made along the Christchurch parallel. Owing to the lack of stations to the east of New Zealand, measurements in that direction were necessarily very approximate. If there are eight waves of equal length in the circuit of the globe, the length of each wave will be 45° of longitude and the distances measured from the wave crests will vary between $+25^{\circ}$ and

* Kidson, 'Commonwealth Bur. Meteorol.,' Bull. 17. Kidson, 'Quart. J. R. Met. Soc.,' vol. 54, p. 27 (1928).

— 25°, the minus sign indicating that the measurement is from a crest to the eastward, and *vice versa*. The waves do not always appear to be of this average length and the distances actually measured varied from + 30° to — 27°.

The ozone values were next collected into groups, each group corresponding to a zone 5° wide in the pressure wave, the centres of the zones being at 0°, + 5°, + 10°, etc. The mean departure of the ozone values from the monthly means was then calculated for each zone. The results are given in Table III, where, however, all positive distances greater than + 27° have been included in the + 30° group. The pressure and temperature departures for the same groups were derived in a similar way and are also given in Table III.

Table III.—Distribution in Pressure Wave.

Zone.	Ozone.	Pressure.	Temperature.	Number of observations.
	0.001 cm.	0.01 inch.	° F.	
0	— 6	+ 24	— 2.5	18
+ 5	+ 2	+ 10	— 1.2	24
+ 10	+ 3	+ 6	— 1.2	20
+ 15	+ 7	+ 5	— 1.6	20
+ 20	+ 8	— 3	— 1.9	10
+ 25	+ 6	— 16	— 1.1	10
+ 30	+ 15	— 40	+ 1.9	9
— 25	0	— 22	+ 3.2	8
— 20	— 7	— 18	+ 3.9	9
— 15	— 8	— 8	+ 3.5	21
— 10	— 5	+ 9	+ 0.5	13
— 5	— 5	+ 3	+ 0.9	11

If the wave in the upper air is similar to that in the lower levels in temperate latitudes, it will consist of a zone of south-westerly winds sweeping round the earth from west to east, their front lying along the line of lowest pressure, followed by a zone of north-westerlies. The greatest velocities will be along, or near the trough line while they will decrease outwards towards the crest of the wave or line of highest pressure. The air just in rear of the trough line will, therefore, have the most pronounced polar characteristics. These will fall off, at first slowly and then more rapidly, until the crest of the wave is reached. Next will be encountered the oldest equatorial air, and the equatorial properties of the air will increase thence onwards towards the trough line, just as did the polar properties. As a wave passes over a station, therefore, from crest to crest, one would expect the amount of ozone to vary as follows: First the values would be about normal and then there would be increasing negative values until the trough line was reached. Here there would be a

sudden change in sign to the highest positive values. These would then decrease, at first slowly and then more rapidly, to about normal at the next crest. This is in accordance with the results given in Table III. They suggest, however, that the amount of ozone is fairly uniform, on the average, in all parts of the polar and equatorial air, respectively. This should be the case if the solar radiation were slow in its effect. Near the crest line there would probably be some mixing of polar and equatorial air and the differences would be smoothed out.

As was previously mentioned, then, the Christchurch observations tend to confirm Dobson's conclusions. They provide, also, an interesting confirmation of the view, which had been arrived at by the writer on other grounds, that the pressure changes in the Australian and New Zealand region are controlled principally by waves at very high levels in the upper air.

The figures in Table III would indicate that the phase in highest levels is slightly in advance of that in the lower layers. The temperature variations at the surface are similar to those of ozone amount but lag behind them. This is probably due to some extent to the local topography. Pressure has usually been rising for some time at Christchurch before the cold change arrives. Nevertheless, some advance of phase in the upper air is indicated.

There are, of course, irregularities in Table III and many individual observations do not appear to fall in with the above theory. The majority of these exceptions could be explained as being due to distortion of the pressure waves as seen at ground level by local surface effects, the waves in the upper air being much more regular. On some occasions, however, irregularities in the upper air are indicated. There are, too, effects for which, with the data available, it is not possible to provide any explanation.

The results for ozone value and temperature given in Table III have been plotted in fig. 4 over a chart showing the normal type of pressure wave. In the figure the values for the $+ 25^\circ$, $+ 30^\circ$ and $- 25^\circ$ zones, have been combined to form one central zone.

If our explanation of the facts is correct, the reason for the apparent lag of the ozone values behind pressure, and the absence of a close correlation will be clear. Owing to the greater contrast between polar and equatorial ozone values in winter and spring than in summer and autumn, the correlation with pressure should be the closer in the former period. The general circulation makes a southward swing in summer and the form of the pressure wave above Christchurch may change somewhat. This may account for the effect referred to towards the end of the third section of this paper."

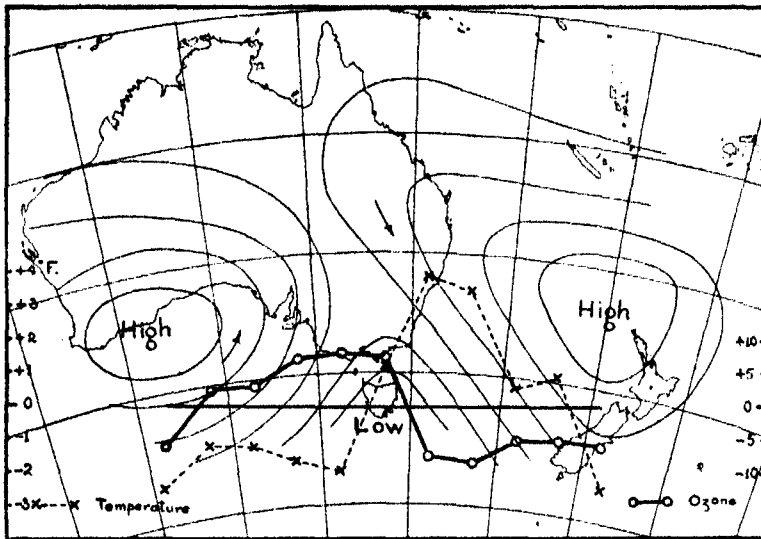


FIG. 4.—Variations of Ozone Amount and Temperature at Christchurch during Passage of typical Pressure Wave.

Egypt.—The absence of well-developed cyclones or anticyclones in this region, together with the lack of meteorological data both to the south-east and south-west, makes it difficult to reach definite conclusions about the connection between the amount of ozone and the pressure conditions here. On the whole it seems that the same relationship holds as in Europe, well marked northerly air currents in the troposphere being associated with much ozone while anticyclonic conditions have little ozone. It is also worth notice that the rise of the ozone value associated with northerly currents seems to be nearly as great in the autumn as in spring in spite of the fact that the change of ozone with latitude is about four times as great in spring as in autumn, which is against the idea of a simple transportation of ozone by the air currents.

India.—Owing to the very constant pressure conditions at Kodaikanal it is not possible to say what the connection would be here, as during the year of observations neither the ozone nor pressure varied by more than a very small amount. The one point of great importance is that there is no marked change in the amount of ozone with the change in the monsoon.

Mean Height of the Ozone Layer.

Some 17 fairly satisfactory observations of the mean height of the ozone layer have been made at Table Mountain, California, using the same method

as was used for the Arosa results.* These indicate a height of between 45 km. and 50 km. which is in agreement with the height found at Arosa. The observations are not, however, very trustworthy so that no great reliance can be placed on them. Observations for the height of the layer at other stations did not give reliable values.

Conclusion.

With the completion of the work described in this paper, the original programme of measurements of the amount of ozone in the atmosphere, which was begun some five years ago, is brought to a close. We have now a general knowledge of the changes in the amount of ozone associated with changes in the pressure distribution in temperate regions and also of the average distribution of the amount of ozone over the world at different times of the year. It may, therefore, be appropriate to recall the reasons why the research was originally undertaken. It was known from the work of Fabry and Buisson that a considerable portion of the sun's ultra-violet energy was absorbed by ozone in the atmosphere and it was believed that this ozone was situated well above the earth's surface. It had also been shown by Prof. F. A. Lindemann and the writer that the temperature of the extreme upper atmosphere is much higher than that at lower levels. This high temperature was explained by the absorption of solar energy by the ozone. The further suggestion was also made by Prof. Lindemann that changes in the temperature of the upper atmosphere, following changes in the amount of ozone, might be the cause of the variations of the pressure at the earth's surface which, in temperate regions, take the form of cyclones and anticyclones. The first observations at Oxford in 1925 showed a marked connection between the ozone and the pressure which was such as would be expected from Lindemann's hypothesis. It thus became very desirable to extend the observations, and it will be seen that the results are still mainly in qualitative agreement with the Lindemann hypothesis.

The following is a brief résumé of the results obtained from both our own and other researches. The distribution of ozone in regions occupied by cyclones or anticyclones was shown graphically in figs. 1 and 2 of our last paper,† while the average distribution over the world is shown in figs. 1 and 2 of the present paper.

* 'Proc. Roy. Soc.,' A, vol. 120, p. 252 (1928), and A, vol. 125, p. 292 (1929).

† 'Proc. Roy. Soc.,' A, vol. 122, p. 456 (1929).

In temperate latitudes the difference in the amount of ozone from its monthly mean is found to be :—

- (1) Slightly correlated negatively with the absolute surface pressure.
- (2) Closely correlated negatively with the pressure at 9 to 16 km. (observations are not available for greater heights).
- (3) Closely correlated negatively with the mean temperature of the troposphere.
- (4) Closely correlated negatively with the density of the air about 15 km. (as shown by Dr. Duckert).
- (5) Fairly closely correlated negatively with the height of the base of the stratosphere.
- (6) Slightly correlated positively with the temperature in the stratosphere.
- (7) Closely related to the surface pressure distribution.
- (8) Closely related to the origin of the air currents in the upper troposphere. (Equatorial currents have little, and polar currents much ozone.)

With regard to the height of the ozone in the atmosphere, several series of observations by different observers all indicate that the height of the centre of gravity of the layer is about 45 to 50 km.* above the surface of the earth. A long series of observations by Dr. Götz at Arosa also indicates that there is little change in the height either with changes in the amount of ozone or with the time of the year. The height is certainly as great at times when there is much ozone as when there is little.

There remain two primary questions regarding the atmospheric ozone which urgently require solution, viz. :—

- (1) What are the chief ozone forming and destroying agents in the atmosphere ?
- (2) What causes the connection between the ozone high in the atmosphere and the meteorological conditions much lower down ?

Let us consider these in detail.

* In the paper giving the observations of the height of the ozone in the atmosphere we have been careful to point out that in calculating the height it is necessary to assume that there is no regular daily variation of the amount of ozone. This assumption has recently been confirmed by the work of M. Chalonge and Dr. Götz at Arosa, as they found from measurements made by moonlight, that the amount of ozone was almost identical by day and by night.

The high temperature of the atmosphere at a height of some 50 km. or more which has been shown by observations of meteors and sound waves, requires that there be a large amount of ozone at these heights, to cause the absorption of sunlight which gives rise to the high temperature.

With regard to the first, the only possible methods whereby ozone might be formed in the atmosphere seem to be :—

- (a) The action of solar ultra-violet radiation of wave-length shorter than about 1850 Å.
- (b) Corpuscular radiation from the sun, including the action of electric fields which may be set up in the atmosphere by such radiation.
- (c) Penetrating radiation.

Of these (c) can easily be shown from Millikan's work to have far too little energy.

The only possible methods by which ozone might be destroyed in the atmosphere seem to be :—

- (d) The action of solar radiation of wave-lengths between 3300 Å. and 2200 Å.
- (e) Reduction by hydrogen or other oxidisable gases in the atmosphere.
- (f) Normal thermal decomposition.
- (g) Catalytic action on the surface of dust particles or nuclei in the atmosphere.

Of these (e) can probably be neglected owing to the very small amount of hydrogen in the atmosphere at the heights in question. With regard to (g), it is difficult to say how great the action might be, but unless it be found that the amount of ozone is markedly decreased after a volcanic eruption has thrown extra quantities of dust into the upper atmosphere, it may probably be neglected in view of the small amount of dust normally present at such great heights.

When oxygen is exposed to sunlight there must be a certain amount of ozone present which is in equilibrium under the actions of (a) and (d). The energy available for (d) is about 100 times as great as that for (a), but it does not necessarily follow that the equilibrium amount of ozone will be very small. We do not know the efficiency of the photo-electric effect and owing to the small concentration of O_3 compared to O_2 (about 1 to 1000 at 50 km.) many O atoms formed by decomposition of O_3 may unite again with O_2 molecules to reform O_3 before meeting either an O_3 molecule or an O atom whereby O_3 might be formed.

It is an obvious suggestion that the constant amount of ozone (about 0.2 cm.) which is apparently found at all times within the tropics, is the amount which is in equilibrium under the actions (a) and (d). Unfortunately we have as yet no observations in polar regions during the winter, but from the curves

of fig. 1 one would expect that the amount of ozone increased rapidly during the polar night. Unless the ozone is transported to the poles and concentrated there by the currents of the general atmospheric circulation, the only action which can increase the ozone at the poles during the dark seems to be (b). We must, therefore, regard it as being the chief ozone-forming agent at the poles and possibly for the world.

In our previous papers we had assumed that the temperature of the upper atmosphere was not likely to be more than 350 A, and we showed that in this case the thermal decomposition was negligible. The recent calculations of Gowan* show that a much higher temperature is probable, in which case the thermal decomposition will be much more rapid and may be important. The temperature will naturally be highest in the summer and so the decomposition will be most rapid in this season also. It thus appears that the decomposition of ozone may be due to either (d) or (f), both of which will produce a similar annual variation except that (f) will lag somewhat after (d).

The second outstanding problem is to explain the close connection between the ozone at a height of some 50 km. and the meteorological conditions much lower in the atmosphere. There appear to be only three ways in which the amount of ozone above a given locality may change, viz. :—

(A) By the transport of large masses of the atmosphere from regions where the amount of ozone is normally large to regions where it is normally smaller (and *vice versa*). Such large air currents are well known in the lower atmosphere in the polar and equatorial currents associated with cyclones.

(B) By vertical currents in the atmosphere immediately above or below the ozone layer which would cause an inward or outward radial flow in the ozone layer itself. The thickness of the ozone layer would thus be increased or diminished.

(C) By actual formation or decomposition of ozone above the area in question.

At first sight (A) appears to be much the most probable and many people have already suggested that this is the real cause. Polar air currents in the upper troposphere are closely associated with high ozone values, and the average ozone content for the whole year is undoubtedly greater at the poles than anywhere else. There are, however, two strong arguments against this view :—

(1) It will be seen from fig. 2 that during the months of July and August, and probably also during September and October, there is very little change

* 'Proc. Roy. Soc.,' A, vol. 128, p. 531 (1930).

of ozone with latitude north of 50° N., and that the values in these latitudes are not more than 0.06 cm. higher than the value at the equator. The values that are associated with cyclones in the region of the British Isles rise much above the average values in polar regions at the same time of year, as the following table will show :—

Month :	July.	August.	September.
Probable average value of ozone in polar regions	cm. 0.290	cm. 0.265	cm. 0.250
Highest ozone value observed in cyclones in N.W. Europe	0.320	0.310	0.290

It is thus clear that at this season of the year (A) will not account for the high ozone values associated with cyclones.

(2) The difference between the average ozone content at the poles and at the equator is about four times as great in the spring as in the autumn. If the ozone variations in temperate regions were caused by the transport of the ozone layer by polar or equatorial currents, the variations of ozone associated with pressure changes should be about four times as great in the spring as in the autumn. Actually the observed ozone variations are almost as great in autumn as in spring, so that again this cause seems ruled out.

It does not seem possible to dismiss cause (B) with certainty, but as the average height of the ozone does not change appreciably with the amount present, it appears very unlikely that this is the cause. It is true that the radiation equilibrium temperature of the layers at a height of about 30 to 40 km., where the absorption and radiation by water vapour is the most important factor, must depend to some extent on the temperature of the layers much lower down, so temperature changes low down may result in vertical currents at a much greater height. It does not seem possible, however, that they should cause such a system of vertical currents as would be necessary to give an increase in the amount of ozone without any change of height.

Even with solution (C) there are difficulties. The total solar energy absorbed by the ozone (for vertical sun) when there is as much as 4 mm. of ozone present is about 6.7 per cent. of that received by the outside of the atmosphere; while when the ozone is only equal to 2 mm. about 5.6 per cent. is absorbed. When the sun is at a lower altitude the difference in the two cases is still smaller. Also the work of Gowan has shown that if there is a uniform percentage increase in the amount of ozone throughout the layer, the increased absorption

of solar energy will occur chiefly in the upper part of the ozonised layer, and the temperature will not change much below a height of about 70 km. It is generally accepted that the energy of cyclones comes from the polar and equatorial air currents associated with them. If this is so and we accept (C) as being true it must act by exerting some "trigger" action.

Whatever the final solution of the problem presented by the ozone-pressure relationship, it appears very desirable to repeat in a much fuller manner the study of the daily distribution of ozone over N.W. Europe which was made in 1926-27. In this way we may perhaps get some further insight into the large-scale meteorological changes which are so important a factor in the weather conditions of temperate latitudes. The photographic instruments which have been used by us in the past have the great disadvantage that the development and measurement of the plates entails much work and great loss of time before the ozone value is known. Further, observations are not possible on cloudy days. For these reasons it has been found necessary to develop an improved type of instrument, and it is hoped that a photo-electric spectrophotometer, now being tested, will prove much superior to the old photographic instruments.

Acknowledgments.

As in the previous papers of this series, the work here described has only been made possible by the co-operation of our many friends in different parts of the world. The actual observations have been made by Dr. Coleridge Farr, F.R.S., in New Zealand; by Dr. Royds and Dr. Narayan, at Kodaikanal, with the permission of the Director-General of Observatories in India; by Dr. Madwah at Helwan, with the permission of the Director of Physical Services in Egypt; while Dr. Götz has continued his unbroken series of observations for three years at Arosa. The Director of the London Meteorological Office and the Instrument Department have again given us much help in arranging for all the transport of the instruments, while the discussions of Prof. Kimball and Dr. Kidson form a most important part of the paper.

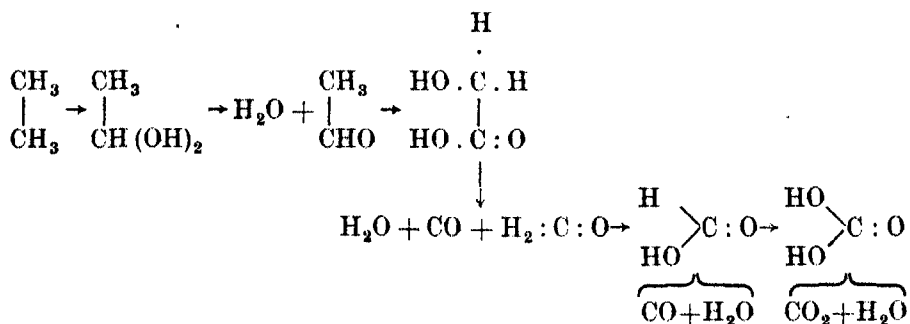
The work has been financed by a grant from the Royal Society for apparatus and general expenses, and by a grant from the Department of Scientific and Industrial Research for clerical assistance. Finally the whole of the measurements of the photographic plates and the calculation of the ozone values, together with the work of preparing the tables and figures for the press, has been done, as previously, by Mr. R. W. M. Gibbs. It is a great pleasure to acknowledge help from all these sources.

The Slow Combustion of Ethane.

By WILLIAM A. BONE, D.Sc., F.R.S., and S. GERALD HILL, B.Sc., A.R.C.S.,
D.I.C.

(Received July 25, 1930.)

The slow combustion of ethane was experimentally studied by W. A. Bone and W. E. Stockings more than 25 years ago,* and shown to proceed in successive stages of hydroxylation, thus :—



Interest in the subject has recently been revived, chiefly because of the conception of "chain reactions," which (to quote a leading exponent) "are now generally supposed to occur whenever many molecules are transformed per quantum in a photochemical change," and of the supposition that "in the combustion of hydrocarbons bodies of a peroxide character are formed and that these act as centres from which chains are propagated."†

The mechanism of hydrocarbon combustion was fully discussed in Chapters XXVIII to XXX (pp. 354 to 400) of Bone and Townend's "Flame and Combustion in Gases" (1927), especially in relation to H. L. Callendar's conclusion (from experiments on hexane and higher hydrocarbons) that the initial stage involves the formation of an alkyl peroxide (rather than of an alcohol) "by the direct incorporation of the oxygen molecules in the hydrocarbon molecule and after direct collision," such peroxide subsequently giving rise to aldehydes and water as decomposition products.‡ It was shown that while the two views are not

* 'J. Chem. Soc.,' vol. 85, p. 693 (1904).

† C. N. Hinshelwood, "Kinetics of Chemical Changes in Gaseous Systems," 2nd ed. pp. 166 and 172 (1929); see also Egerton and Gates, 'J. Inst. Petr. Tech.,' vol. 13, p. 281 (1927).

‡ 'Engineering,' vol. 123, pp. 147-8, 182-4, 210-2 (1927).

mutually exclusive, and may perhaps even be supplementary, "hydroxylation" explains most of the known facts better than "peroxidation." This conclusion was strengthened by the results of Dr. D. T. A. Townend's experiments on the partial combustion of methane at high initial pressures which, while quite understandable from the point of view of "hydroxylation," seem incompatible with the idea of a primary peroxide formation.* Also, it may be mentioned that in 1928 M. Stanislas Landa, in describing the results of his experimental study of the slow combustion of higher paraffins at 280 to 300°C., reported having isolated alcohols as well as aldehydes from the products in accordance with the "hydroxylation" theory.†

In the paper entitled "Kinetics of the Oxidation of Ethylene," communicated to the Society about a year ago by H. W. Thompson and C. N. Hinshelwood,‡ a *via media* between the two views was reached. Starting from the submission that "the idea of chain reaction has long been familiar in connection with photometrical changes, but experimental evidence that thermal changes sometimes occur by a chain mechanism has only recently been forthcoming," and that "the conditions are particularly favourable to the operation of this chain mechanism in highly endothermic gaseous reactions" (p. 277), it went on to describe experiments on the interaction of ethylene-oxygen mixtures (but chiefly $C_2H_4 + O_2$ and $C_2H_4 + 2O_2$) in silica bulbs between 400 and 500°C., and concluded by saying (p. 291) that (i) in such circumstances the oxidation is "probably a chain reaction," the rate being affected by the total pressure "approximately as a reaction of the third order, the effect depending very much more on the partial pressure of the ethylene than of the oxygen," and (ii) while "the first stage of the reaction is the formation of a stable peroxide;" yet "if this reacts with more oxygen the chain ends, but if it reacts with ethylene unstable hydroxylated molecules are formed which continue the chain," so that (iii) "on the other hand, there is no doubt that Bone's interpretation of the complete course of oxidation as process of successive hydroxylation is essentially correct," the two views being not incompatible and in combination capable of explaining all the facts.

Thus, for example, it was supposed "that the initial act in the oxidation is a collision between ethylene and oxygen giving the unstable $C_2H_4O_2$. If this collides with another ethylene molecule the oxygen is shared and two hydroxy-

* 'Proc. Roy. Soc.,' A, vol. 116 (1927), pp. 637-663, and "Gaseous Combustion at High Pressures" (Bone, Newitt and Townend), chap. 18, p. 271 to 299 (1929)

† 'Compt. Rend.,' vol. 186, p. 539 (1928).

‡ 'Proc. Roy. Soc.,' A, vol. 125, pp. 277 to 291 (1929).

lated molecules, e.g., $\begin{array}{c} \text{CHOH} \\ | \\ \text{CH}_2 \end{array}$, are produced, which continue the chain. If, how-

ever, the peroxide collides with oxygen it may either be decomposed or oxidised completely to stable products which do not happen to be effective in continuing the chain."

While it may be pleasing to have the two view points thus reconciled, and generally agreeable that the reactions involved have the characteristics of "chain reactions," there is more difficulty in deciding as to what is the *initial* oxidation product in any particular case; and the existing experimental evidence of an initial "peroxidation" does not seem to us at all convincing.

For here a caveat may be lodged. It is not enough to show, as some have done, that during the slow oxidation of a hydrocarbon products are formed capable of liberating iodine from a solution of potassium iodide, because (at least in presence of oxygen) aldehydes will do it, so that all such evidence may at once be ruled out. Indeed the only evidence which should really count is that of a reagent, such as a solution of titanous sulphate, which will unequivocally show "peroxide" and nothing else. Neither would it suffice to show the formation of some unidentified "peroxide" during the combustion process without at the same time proving both that it really is an *initial* product, and not merely a peroxide incidentally formed during the further oxidation of, say, acetaldehyde. Otherwise there would be a danger of mistaking a later by-product in the reaction sequence for its initial one; as will be seen later, such danger undoubtedly exists in the case of the oxidation of ethane.

For the satisfactory decision of the point we would require either the unimpeachable identification of the *initial* oxidation product during an experiment or, failing it, at least such a combination of simultaneous pressure and analytical data as will enable complete carbon-hydrogen-oxygen balances being deduced at various selected points during its course, and so far such evidence has been wanting.

It may be recalled that the earlier experiments of Bone and Stockings (1904) upon the slow combustion of ethane comprised principally two distinct series, namely, in which (i) a series of homogeneous $2\text{C}_2\text{H}_6 + \text{O}_2$, $\text{C}_2\text{H}_6 + \text{O}_2$, $\text{C}_2\text{H}_6 + 2\text{O}_2$, $\text{C}_2\text{H}_6 + 3\frac{1}{2}\text{O}_2$, etc. mixtures were sealed up at room temperature and pressure in cylindrical borosilicate glass bulbs (capacity = *circa* 80 c.c.) each of which were afterwards kept for a definite time at some constant temperature between 250 and 400° C. so that reaction would occur at some pressure between 1.75 and 2.33 atmospheres; and (ii) either $2\text{C}_2\text{H}_6 + \text{O}_2$ or $\text{C}_2\text{H}_6 + \text{O}_2$.

mixtures were continually circulated in a closed system comprising a "reaction tube," packed with fragments of porous porcelain and maintained at a constant temperature of 450° or 500°, suitable cooling and condensing arrangements to ensure the rapid removal of condensible and soluble products, and a manometer. Comparative circulation experiments were also made upon the slow combustion of ethyl alcohol and acetaldehyde, respectively.

The principal results showed, *inter alia*, that (i) the oxidation proceeds in stages, without any deposition of carbon or liberation of hydrogen, the oxygen being initially incorporated in the hydrocarbon molecule forming an oxygenated product; (ii) while there was but little to choose between the rates of reaction of $2\text{C}_2\text{H}_6 + \text{O}_2$ and $\text{C}_2\text{H}_6 + \text{O}_2$ mixtures, respectively, any increase of oxygen beyond the equimolecular proportion greatly retarded the process; (iii) acetaldehyde and steam are simultaneously formed at an early, and formaldehyde, together with carbonic oxide and more steam, at a subsequent stage; (iv) considerable proportions of carbon dioxide were always produced in circumstances precluding its arising from a secondary oxidation of carbonic oxide; and (v) an undue accumulation in the system of aldehyde, but more particularly of acetaldehyde, in a reacting $\text{C}_2\text{H}_6 + \text{O}_2$ medium may result in their partial thermal decomposition, or even to a local ignition, with consequent inflammation, occurring. Moreover, while ethyl alcohol was never identified among the reaction products, although diligent research for it was made, its rate of oxidation under the experimental conditions was shown to be much greater than that of ethane. And later on, in connection with the research, when (1906) Dr. Julian Drugman proved the abundant formation of ethyl alcohol (followed by that of acetaldehyde and acetic acid) by subjecting ethane to oxidation by ozone at 100°, any difficulty about regarding it as really the initial oxidation product with oxygen seemed to disappear, so that the primary oxidation of the hydrocarbon might be considered as a "non-stop" run through ethyl alcohol to di-hydroxy ethane, etc.

Similar results were also obtained about the same time (1904) by W. A. Bone and R. V. Wheeler during like experiments upon the slow combustion of ethylene;* in this case, however, conclusive evidence of the early formation of acetaldehyde, presumably arising by inter-molecular change from the unstable monohydroxy-ethylene (vinyl alcohol) $\text{H}_2:\text{C}:\text{CHOH}$, was forthcoming. Some years later (1923) this highly significant fact was independently confirmed during experiments on the "Oxidation of Hydrocarbons with Special References to the Production of Formaldehyde" carried out by Messrs. F. S. Wheeler

* 'J. Chem. Soc.,' vol. 85, p. 1637 (1904).

and E. W. Blair at R.N. Cordite Factory, Holton Heath, for the Chemistry Board of the Department of Scientific and Industrial Research.*

The experiments described in this paper were undertaken with a view of determining, if possible, not only whether or not a peroxide is formed during the slow combustion of ethane, but (if so) then at what stages of the process. Accordingly experimental methods were adopted whereby the oxidation process at a given temperature could be followed throughout by means of pressure records supplemented with analytical data, thus permitting carbon-hydrogen-oxygen balances being drawn up at selected points. Means were devised whereby the partial pressures of acetaldehyde, formaldehyde and peroxide (if any) present in the products at each particular point could be estimated. Unfortunately, for reasons which will be explained later, it was not found possible to devise means whereby the presence (or otherwise) of ethyl alcohol could be directly proved, although certain indirect evidence upon the point was forthcoming.

EXPERIMENTAL.

(1) *General Arrangements.*

Apparatus and Method.—The experimental mixtures— $2\text{C}_2\text{H}_6 + \text{O}_2$, $\text{C}_2\text{H}_6 + \text{O}_2$, $\text{C}_2\text{H}_6 + 2\text{O}_2$, etc.—having been made up accurately in a gas holder over mercury from their highly purified constituents and then analysed, each was separately introduced into the “reaction vessel” A (fig. 1)—a cylindrical bulb (27.5 cm. long, 5 cm. internal diameter, and 586 c.c. capacity) of transparent silica furnished with $\frac{1}{4}$ mm. bore entry and exit tubes—which had been previously heated to the desired constant experimental temperature in the electric resistance furnace B and thereupon evacuated. This “reaction vessel” had suitable external connections (as shown in the diagram), on the one hand through the glass stop cock T_1 with (if need be) some receptacle containing any “third body” whose influence upon the combustion it was wished to study, and, on the other, through the three-way stop cock T_2 (one limb of which served for gas sampling purposes), with the manometer C, and thence through a third stop cock T_3 with the gas-holder containing the experimental mixture, and with a hyvac pump. In “dry” experiments, the interior of A had been previously well dried out, and a 90 cm. long tube of redistilled phosphoric anhydride was inserted between the gas holder and the stop cock T_3 ; otherwise, the interior of A was simply dried out by evacuation at the experimental temperature and the experimental mixture introduced into it “moist” (i.e., saturated at $15^\circ\text{C}.$)

* ‘J. Soc. Chem. Ind.’ vol. 41, p. 303T (1922) and vol. 42, pp. 81, 87, 415T (1923).

from the gas-holder. Any tendency for condensation of water or other liquid in the "capillary" connection between T_1 and T_2 during an experiment was

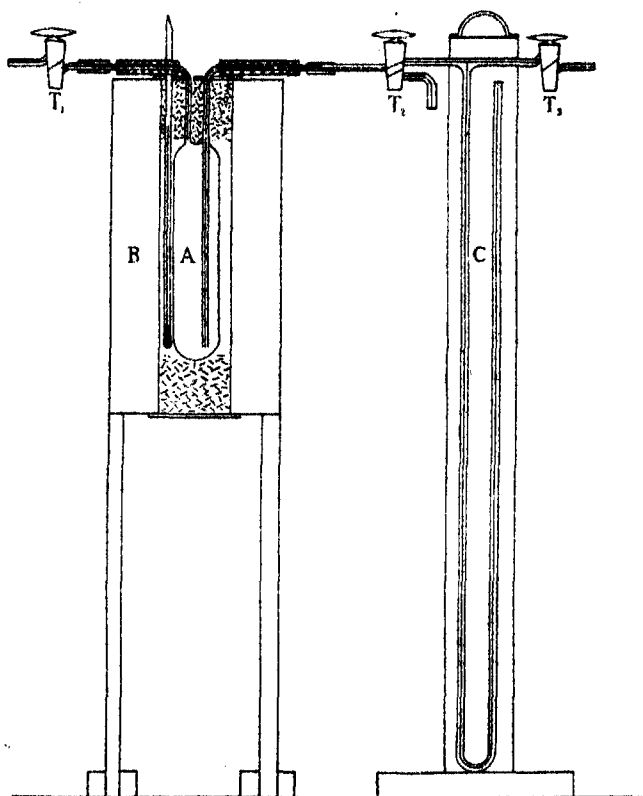


FIG. 1.

prevented by keeping them at about 150°C . by means of an electrically heated nichrome wire. Arrangements were also made whereby, if and when desired, the reaction vessel and its contents could be suddenly cooled at any moment by plunging them into a mixture of ice and water so that the reaction would be stopped and water and other condensable or soluble products (*e.g.*, alcohol, aldehydes, peroxides, etc.) would be condensed as far as possible out of the system. And after removing therefrom a sample of the gaseous products for analysis, the contents of the so-cooled vessel were shaken and rinsed out with a measured volume (about 20 c.c.) of distilled water whereby such condensable or soluble products could be removed in aqueous solution for examination and estimation.

It was thus possible (i) to fill the reaction vessel at any desired pressure and

temperature with any given experimental mixture of ethane and oxygen; (ii) if desired, to add thereto a known small proportion of any other gas or vapour; (iii) to follow the course of the reaction throughout by pressure readings; (iv) to stop it suddenly at any desired moment, "freeze out" condensable and soluble products at 0°C ., and subsequently remove them in solution so as to permit of their identification and estimation being undertaken, and (v) at any desired moment to withdraw a sample of the gaseous products from the system.

Tabulation of Results.—Perhaps the best way of tabulating the experimental results will be to ignore any adventitious nitrogen (always less than 2 per cent.) as well as moisture (if any) originally present in the system, and to record only the partial pressures of the gaseous or vapourised reactants or products, either at the experimental temperature or at 0°C . as the case may be. For we shall thus get comparative views of the state of the system, not only at the beginning and end of the oxidation process, but also at various intermediate points.

Pressure Time Curves.—In many cases the experimental results can best be presented in the form of pressure-time curves, in which *either* the total pressure of the system (as actually recorded by the manometer) or the partial pressures of its various constituents at the particular experimental temperature are plotted as ordinates against time (in minutes) as abscissa.

(2) *The Detection and Estimation of Condensable and Soluble Intermediate Products.*

As ethyl alcohol, acetaldehyde and formaldehyde, as well as "peroxide" and formic acid might conceivably be present in the system at any moment during an experiment, it was necessary to devise suitable means for (if need be) separately detecting and estimating each, and this involved quite a research in itself. Without going into details, we may briefly indicate in principle the methods finally adopted as being the best for our purpose.

Peroxide.—The amount of peroxide in a liquid condensate or solution (aqueous rinsings) was estimated colorimetrically by means of a 5 per cent. solution of titanous sulphate in 5 per cent. sulphuric acid, using a $\text{N}/40$ aqueous solution of hydrogen peroxide as a standard. Careful experiments showed that, when properly applied, this method yields accurate quantitative results, and is easily capable of detecting 1 part of peroxide in 500,000 of water. We were thus usually able both to detect and to estimate any small amount of "peroxide" among the intermediate oxidation-products; and as its formation was always concomitant with that of aldehydes (and more particularly of acetalde-

hyde), for purposes of calculation we have regarded it as most probably an unstable $C_2H_4O_3$.

Aldehydes.—As both acetaldehyde and formaldehyde were nearly always present in the reacting media, we first of all applied reliable qualitative tests for each, and (on finding both) next proceeded to estimate (i) the formaldehyde by means of Romijn's potassium cyanide method, which is sensitive to 1 part in 100,000, and then (ii) the total aldehydes by means of Ripper's bisulphite method, which is equally sensitive. The difference between (ii) and (i) was taken as a measure of the acetaldehyde present.

Acid.—In many cases inconsiderable amounts of an organic acid were present; this was estimated by titration with N/100 alkali and for the purposes of calculation reckoned as formic acid.

Ethyl Alcohol.—The detection of small amounts of ethyl alcohol in a solution containing acetaldehyde, and maybe formaldehyde, also is difficult. Both ethyl alcohol and acetaldehyde give the iodoform reaction; but whereas with aqueous acetaldehyde alone the precipitate is amorphous and the sensitivity of the test 1 in 5000, in the case of aqueous ethyl alcohol alone the precipitate is crystalline and the sensitivity only 1 in 2000. When, however, both are present together in anything like comparable amounts in an aqueous solution, before the ethyl alcohol can be detected with certainty it is necessary first of all to oxidise all the acetaldehyde at room temperature by means of an excess of ammoniacal silver solution (1 hour), then to acidify the liquid with dilute sulphuric acid, next to subject it to steam distillation, and finally to reapply the iodoform test to the distillate. Unfortunately such procedure reduces (as we found) the sensitivity of the test for alcohol to 1 in 100 on the solution originally taken, which was insufficient for our purpose. Hence, in considering the possible primary formation of ethyl alcohol in our experiments, only indirect evidence can be called in.

(3) General Characteristics of the Oxidation.

Bone and Stockings had observed signs of incipient reaction in a moist equimolecular $C_2H_6 + O_2$ mixture after a week in their borosilicate bulbs at $223^\circ C$. and a pressure of 1.75 atmospheres; and at $250^\circ C$. and 1.85 atmospheres they found reaction to proceed fairly rapidly, in one case the whole of the oxygen disappearing within 17 hours.

The present investigation has covered a temperature range of 290° to 323° and initial pressures between 440 mm. and 780 mm., the temperature usually being 316° and the initial pressure between 720 mm. and 770 mm. Under such

conditions, when once started, reaction proceeded with a velocity that could be conveniently measured by means of the pressure-rise.

Four characteristics of such slow oxidation of ethane were soon manifested, namely that :—(i) it proceeds homogeneously throughout the medium, being greatly retarded by increasing the surface exposed to the gases (*e.g.*, by packing the reaction vessel with fragments of transparent silica) ; (ii) it is preceded by a well-marked “induction period” ; (iii) its rate is largely governed by the ethane-concentration, being always much greater for a $2\text{C}_2\text{H}_6 + \text{O}_2$ than for a $\text{C}_2\text{H}_6 + \text{O}_2$ mixture ; and (iv) it is accompanied by a steady pressure rise (all products being kept within the reaction zone), and the production chiefly of aldehydes, steam, oxides of carbon, but of neither hydrogen nor free carbon. On subsequently cooling the system down to 0°C . the steam, aldehyde, etc., condensed, causing the pressure to fall below what would have been that of the original mixture at the same temperature. These points will now be considered in detail.

(4) *The Induction Period.*

Proof.—The first thing which struck an observer watching our experiments was the fact that in every case a considerable time elapsed between the introduction of the gaseous mixture into the reaction vessel and the commencement of any pressure-rise. Thus, for example, on filling the reaction vessel (previously well dried out) at 316°C . and 718 mm. with a *dry* equimolecular $\text{C}_2\text{H}_6 + \text{O}_2$ mixture, nothing happened during the next 30 minutes to cause any perceptible movement in the manometer, and an analysis of the medium at the end thereof showed it to be unchanged, save for the presence of negligibly small amounts of oxides of carbon. Thus, in one instance, a mixture originally containing :—

$$\text{C}_2\text{H}_6 = 49.2 \text{ and } \text{O}_2 = 50.8 \text{ per cent.},$$

having been introduced into the reaction vessel at 316° and 717 mm., at the end of 27 minutes it was found to contain :—

$$\text{C}_2\text{H}_6 = 48.9, \text{ O}_2 = 50.6, \text{ CO}_2 = 0.1, \text{ and CO} = 0.4 \text{ per cent.},$$

no trace of “peroxide” being present. After about 30 minutes, however, a steady pressure rise (indicative of oxidation) set in, at first rather slowly (30 to 60 minutes), but afterwards more rapidly (60 to 90 minutes), until by the end of 100 minutes, or thereabouts, from the start of the experiment the pressure became steady again at 868 mm., the ratio p_f/p_i being 1.21. The pressure-time curve of one such instructive experiment is shown in fig. 2 (*q.v.*). The

final cold gaseous products contained $\text{CO}_2 = 9.4$, $\text{CO} = 47.8$, $\text{C}_2\text{H}_6 = 36.9$, $\text{C}_2\text{H}_4 = 1.7$, $\text{CH}_4 = \text{nil}$, $\text{H}_2 = 2.3$, and $\text{O}_2 = 1.9$ per cent.

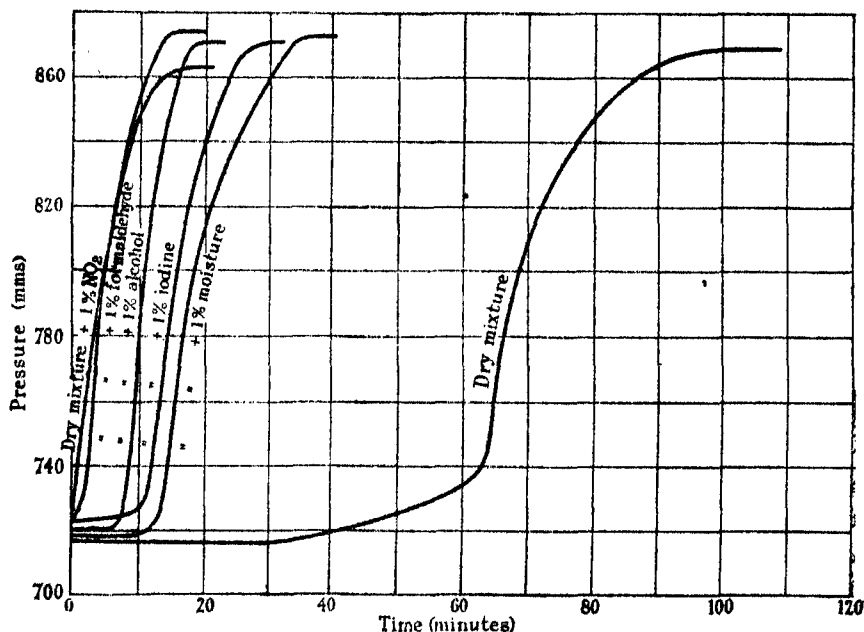


FIG. 2.—Effects of Foreign Substances upon the "Induction" and "Reaction" Periods of Mixture $\text{C}_2\text{H}_6 + \text{O}_2$ at 316° .

We thus learned to distinguish three phases in such an experiment, namely (i) a preliminary "induction period" (in this case about 30 minutes) during which no perceptible oxidation occurred, but the gases (or at least one of them) were merely "getting ready" in some way, followed by (ii) a period (again of about 30 minutes) of oxidation marked by a comparatively slow pressure rise, and finally (iii) a period, also of oxidation, marked by a relatively rapid pressure rise.

Influence of Third Bodies thereon.—At a later stage of the research it was discovered that the "induction period" can be shortened considerably by introducing into a well-dried $\text{C}_2\text{H}_6 + \text{O}_2$ medium, contained in the reaction vessel at 316° and a pressure of 720 mm. to 730 mm., a relatively small volume (say 1 per cent.) of some foreign vapour such, for example, as moisture, iodine, nitrogen peroxide, ethyl alcohol or formaldehyde, all of which also accelerated the subsequent reaction without, however, altering its character as a slow non-explosive oxidation.

These observations are shown in Table I., and illustrated by the pressure time curves shown in fig. 2.

Table I.—Durations of "Induction" and "Reaction" Periods with a dry $C_2H_6 + O_2$ Medium at 316° C. and 720 mm. to 730 mm., and with various additions.

	Induction period	Reaction period
	minutes	minutes
Dry medium <i>only</i>	30	70
" plus 1 per cent. moisture	10	25
" plus 1 per cent. C_2H_5OH	6	18
" plus 1 per cent. iodine	5	25
" plus 1 per cent. NO_2	0	20
" plus 1 per cent. CH_4O	0	20

The introduction of 1 per cent. formaldehyde vapour, for example, entirely obliterated the "induction" period, the pressure rise (from 723 mm. to 877 mm.) commencing immediately and being completed within 20 minutes. The reaction, though rapid, was entirely non-explosive, there being no separation of carbon and the N_2 -free cold gaseous products contained :—

$$CO_2 = 8.5, \quad CO = 46.3, \quad C_2H_6 = 41.3, \quad CH_4 = \text{nil}, \quad H_2 = 3.6, \\ \text{and } O_2 = 0.3 \text{ per cent.}$$

The most striking result of all, however, was obtained on introducing 1 per cent. of acetaldehyde vapour into the dry $C_2H_6 + O_2$ medium at 316° and 710 mm. in the reaction vessel; for the medium was instantly inflamed with a sudden pressure rise to *circa* 1300 mm., and a blackening of the vessel walls with carbon. The final cold gaseous products contained :—

$$CO_2 = 3.9, \quad CO = 30.7, \quad C_2H_2 = 2.5, \quad C_nH_{2n} = 1.0, \quad CH_4 = 12.1, \\ C_2H_6 = 2.2, \quad H_2 = 47.0, \quad \text{and } O_2 = 0.6 \text{ per cent.,}$$

a composition which is characteristic of the explosion products of the mixture.

That the addition of 1 per cent. of ethyl alcohol reduced the "induction" period to about one-fifth and the "reaction" period to less than one-third of the natural duration, and that 1 per cent. of acetaldehyde caused an instantaneous explosion, whereas 1 per cent. formaldehyde vapour caused a rapid non-explosive reaction to set in immediately, are a group of highly significant facts consistent with the hydroxylation theory, indicating the acetaldehyde

stage of the combustion as being probably important from the point of view of "knock." This, however, is a matter which we are reserving for further investigation.

Influence of Various Proportions of Ethane and Oxygen thereon.

Perhaps still more significant were the results of a series of comparative experiments in which moist (saturated at 15° C.) mixtures $2C_2H_6 + O_2$, $C_2H_6 + O_2$, $C_2H_6 + 2O_2$ and $C_2H_6 + 3O_2$ respectively, were each separately introduced into the dry vacuous experimental vessel at 316° C., and initial pressures of 718 mm. to 725 mm., and observations made of the ensuing "induction" and "reaction" periods in each case. These are summarised in the pressure-time curves shown in fig. 3, and Table II.

Table II.—Influence of Mixture Composition upon Durations of "Induction" and "Reaction" Periods.

Moist mixture.	$2C_2H_6 + O_2$.	$C_2H_6 + O_2$.	$C_2H_6 + 2O_2$.	$C_2H_6 + 3O_2$.
Initial pressure at 316° C. (mm.)	724	718	721	718
Maximum final pressure at 316° C. (mm.)	820	870	910	840 and still rising.
Duration of induction period (minutes)	3	30	60	240
Duration of reaction period (minutes)	13	35	225	4320
Percentage composition of cold gaseous end products—				
CO ₂	4.8	9.7	23.6	23.4
CO	26.6	48.2	63.6	45.7
C ₂ H ₆	65.8	38.9	11.6	7.1
H ₂	2.0	2.5	1.1	1.2
O ₂	0.8	0.7	0.1	22.6
Ratio CO/CO ₂	5.5	5.0	2.7	2.0

It is thus manifest that the $2C_2H_6 + O_2$ was by far the most reactive of all the mixtures examined, a fact which while quite consistent with the "hydroxylation" theory, is hardly so with that of "peroxidation"; another noteworthy thing was how rapidly an excess of oxygen beyond an equimolecular proportion retarded the combustion.

Influence of Temperature and Pressure thereon.—In order to ascertain the influence of temperature and pressure upon the duration of the "induction" and "reaction" periods respectively, comparative experiments were made in

which the same moist (saturated at 15° C.) equimolecular $C_2H_6 + O_2$ mixture was introduced into the vacuum reaction vessel either (i) at 318° C. but various

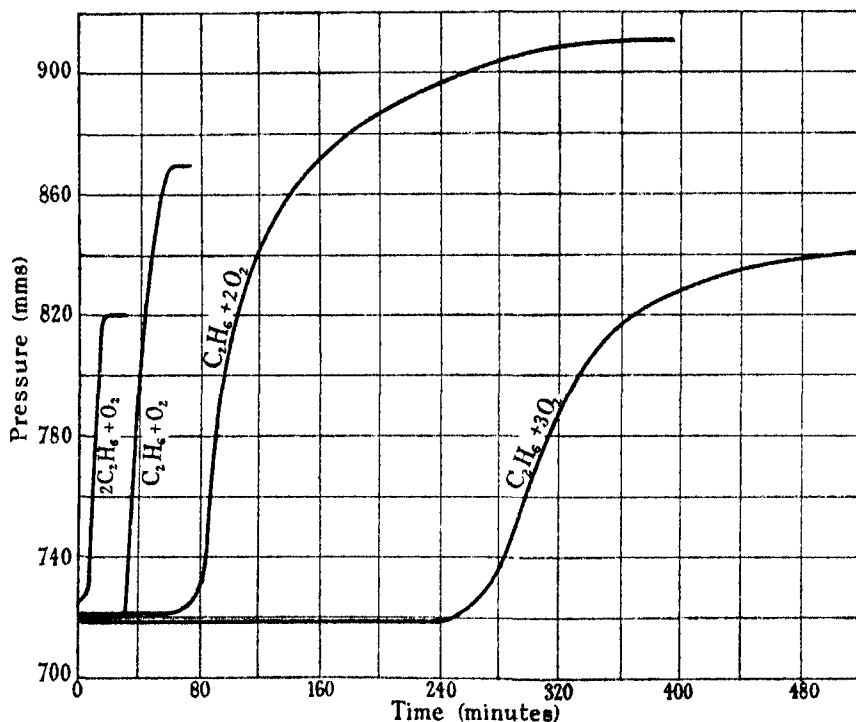


FIG. 3.—Influence of Mixture Composition upon "Induction" and "Reaction" Periods at 316°.

initial pressures between 420 mm., and 770 mm. or (ii) at atmospheric pressure (767 mm. to 775 mm.) but at various temperatures between 290° and 318° C. The results are summarised in the pressure-time curves shown in figs. 4 and 5, and in Tables III and IV.

Table III.—Influence of Initial Pressure at 318° thereon.

Initial pressure.	Approximate durations of	
	Induction period.	Reaction period.
mm.	minutes	minutes
420	73	87
520	48	77
610	30	80
704	20	75
775	15	60

Table IV.—Influence of Initial Temperature at 770 mm. thereon.

Initial temperature.	Approximate durations of	
	Induction period.	Reaction period.
° C.	minutes	minutes
290	90	120
295	50	110
300	33	97
307	18	82
318	15	65

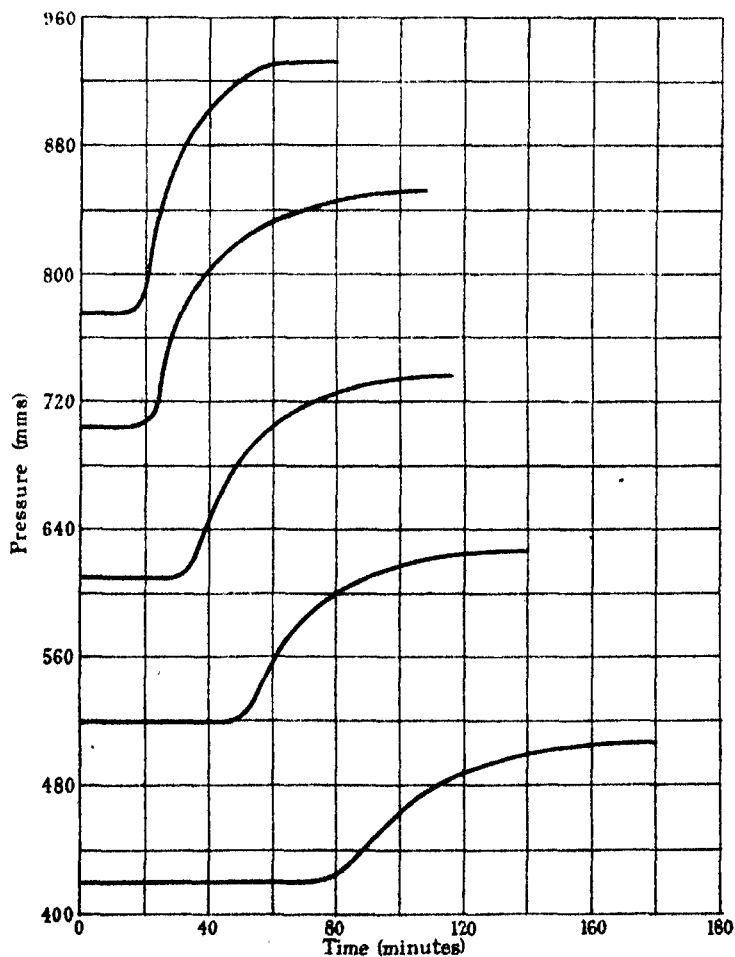


FIG. 4.—Influence of Initial Pressure in the "Induction" and "Reaction" Periods of $C_2H_6 + O_2$ Mixture at 318° .

It is thus seen that the "induction period" was greatly shortened by increase in either pressure or temperature, as was also the "reaction period" by a rise

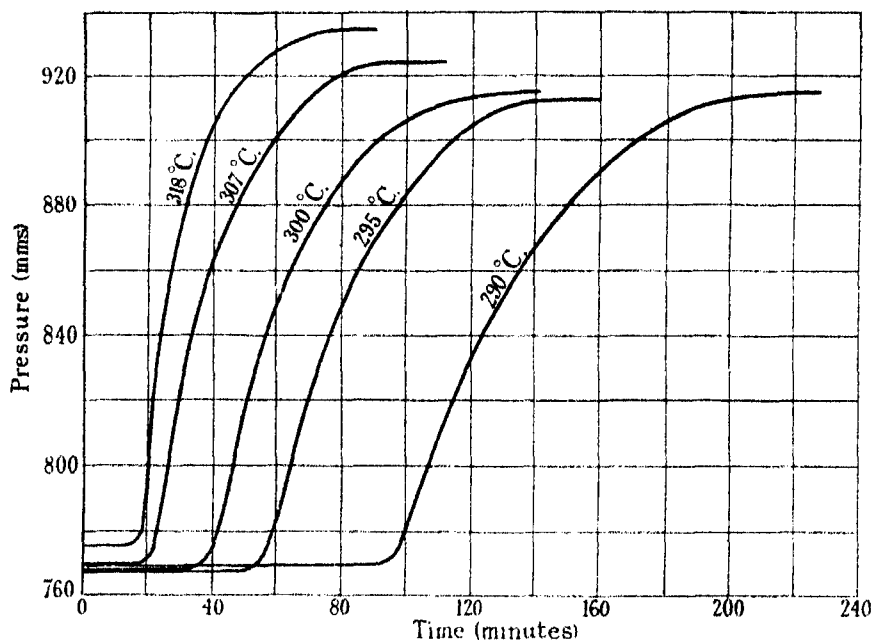


FIG. 5.—Influence of Temperature upon the "Induction" and "Reaction" Periods of $C_2H_6 + O_2$ Mixture at 770 mm.

in temperature; the effect of pressure rise upon the "reaction period," though not very marked within the range explored, on the whole was slightly to shorten it.

(5) Detailed Study of the Initial Stages of the Combustion.

During this part of the work, detailed studies were made of the interactions of mixtures originally containing $2C_2H_6 + O_2$ or $C_2H_6 + O_2$ when introduced into the reaction vessel at 303° to 305° , or 313° to 316° , respectively, with the object of tracing in each case both the rate of disappearance of ethane and oxygen and those at which the various reaction products accumulated.

The experimental method consisted in:—(A) first of all separately introducing each of the two experimental mixtures (moist and saturated at 15°) into the reaction vessel at a pressure of *circa* 720 mm. (= *circa* 690 mm. for the dry N_2 -free gases) and a temperature of 303° to 305° in the case of the $2C_2H_6 + O_2$, but 313° to 316° C. in the case of the $C_2H_6 + O_2$ mixture; afterwards in each case measuring (i) the whole "induction period," and (ii) the pressure-rise at

intervals throughout the subsequent "reaction period"; and finally, when all seemed over, suddenly plunging the reaction vessel into a mixture of ice and water so as to condense out steam and other vapours (aldehydes, peroxide, formic acid, etc.) for examination and estimation as already described, leaving the gaseous products for subsequent analysis; and (B) repeating the procedure several times, but on each occasion stopping the reaction by plunging the vessel into the ice-water mixture at some different predetermined point during the "reaction period,"

Such procedure, supplemented by analyses of the gaseous products, and by quantitative estimation of aldehydes, "peroxide," formic acid, etc., in the manner already described (due allowance being made for their vapour pressures in the rinsings at $0^{\circ}\text{C}.$), enabled a series of carbon-hydrogen-oxygen balances being drawn up for the system at each such selected intermediate point.

To avoid cumbering the story with needless details, all the essential data relating thereto have been set out in Tables V and VI and in the pressure-time curves shown in figs. 6 and 7. In the last-named are plotted, against

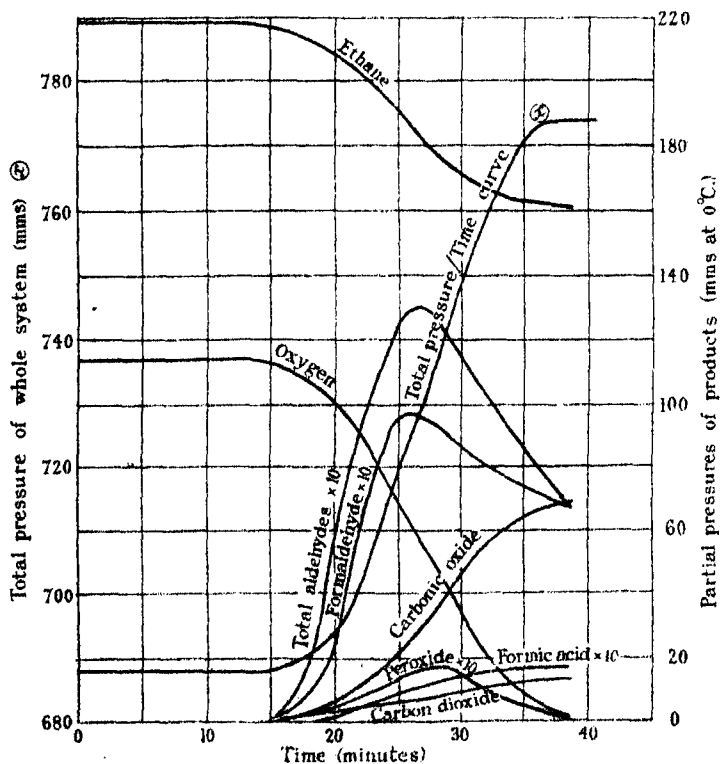


Fig. 6.— $2\text{C}_2\text{H}_6 + \text{O}_2$ Mixture at $303-5^{\circ}$.

time in minutes, not only the total pressure of the medium as a whole in the reaction vessel at the experimental temperature (T°), but also the partial

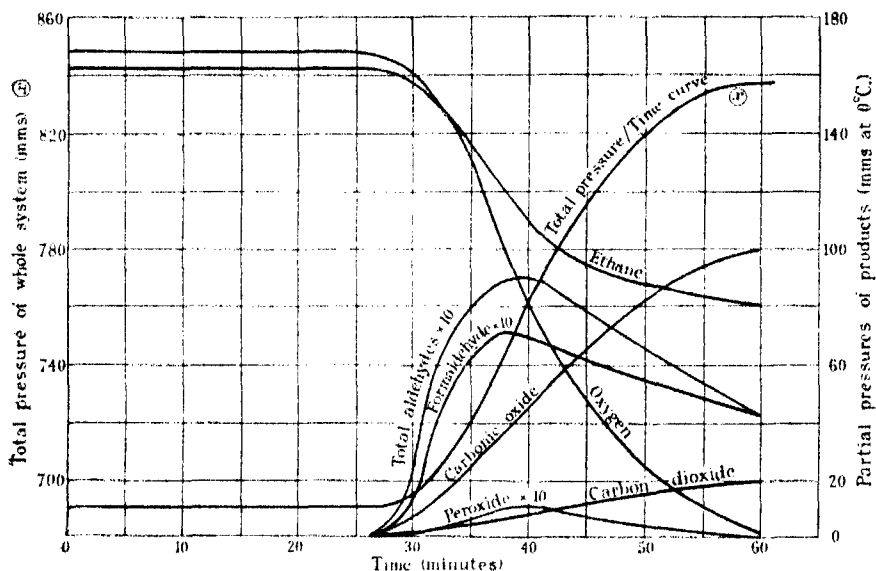


Fig. 7.— $\text{C}_2\text{H}_6 + \text{O}_2$ Mixture at $313\text{--}6^\circ$.

pressure at 0° of the ethane, oxygen, carbon dioxide, carbon monoxide, total aldehydes and formaldehyde (the difference between them = acetaldehyde), "peroxide" (reckoned as $\text{C}_2\text{H}_4\text{O}_3$) and formic acid (if any). *It should, however, be particularly noted that, in order to render the aldehydes, peroxide, and formic acid partial pressure curves more readable, they have been drawn to a 10 times larger scale than those of all the other constituents.*

The outstanding points brought out by this part of the evidence are :—(i) that up to the end of the "induction period" practically no oxidation, and certainly no "peroxidation," of the ethane had taken place, all but a trifling percentage of the original ethane and oxygen remaining intact; (ii) the relative inconsiderableness of any "peroxide" among the products; and (iii) the fact that "peroxide" was never observed except as concomitant with acetaldehyde which it neither preceded nor survived.

The last observation accords well with the one already described in which the introduction of 1 per cent. aldehyde vapour into a dry $\text{C}_2\text{H}_6 + \text{O}_2$ medium at 318° and atmospheric pressure caused an instantaneous "inflammation," and it is supported by the recent work of E. J. Bowen and E. L. Tietz* upon

* 'J. Chem. Soc.', p. 234 (1930).

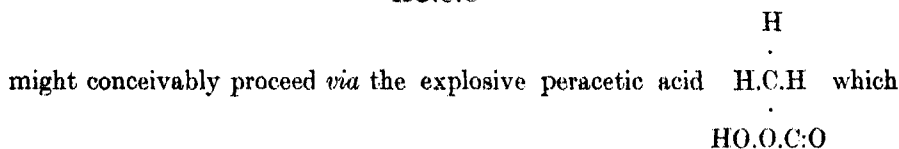
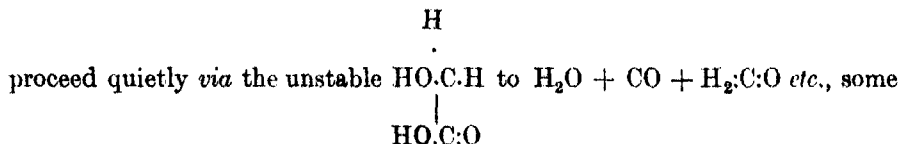
Table V.—Experiments with a $2C_2H_6 + O_2$ Mixture at $T = 303$ to $305^\circ C$.

Time in minutes from start. (induction period = 15 mins.)	(1)	(2)	(3)	(4)	(5)	(6)
Initial pressure of dry mixture at T° mm.	689	679	687	688	688	689
Final pressure of products (including H_2O) at T° mm.	689	689	708	736	757	778
Partial pressures (mm.) in original mixture at $0^\circ C$.—						
C_2H_6	218.5	215.9	216.2	218.6	218.3	218.5
O_2	114.0	112.6	112.8	114.1	113.9	114.0
Partial pressures (mm.) of gaseous products at $0^\circ C$.—						
CO_2	2.3	2.8	4.9	7.6	10.7	12.9
CO	2.7	9.4	22.1	36.6	55.0	68.7
C_2H_6	216.5	204.6	189.8	177.5	167.0	161.1
O_2	111.0	93.7	69.2	48.4	21.3	1.3
Partial pressures (mm.) of aldehydes, peroxide, and formic acid reduced to $0^\circ C$.—						
$CH_3 \cdot CHO$	Nil	2.2	2.5	3.1	1.9	Nil
$H_2 : C : O$	Nil	6.0	9.5	9.1	7.9	6.7
$C_2H_4O_2$	Nil	0.3	1.3	1.8	0.9	Nil
$H \cdot COOH$	Nil	Nil	0.9	1.3	1.6	1.7
Ratio O_2/C_2H_6 used up	—	1.67	1.65	1.9	1.8	1.96
C, H_2, O_2 balance—						
Units in original mixture	437 655 114	432 648 113	432 649 113	437 656 114	437 655 114	437 656 114
Units in above products	438 650 114	432 625 106	424 588 94	420 553 84	415 516 67	412 492 54
Difference = unite as H_2O and " $Oxy-C_2H_4$ "	Nil	0 23 7	8 61 19	17 103 30	22 139 47	25 164 60

Table VI.—Experiments with a $C_2H_6 + O_2$ Mixture at $T = 313$ to $316^\circ C$.

	(1)	(2)	(3)	(4)	(5)
Time in minutes from start. (induction period = 26 mins.)	26	32	34	41	60
Initial pressure of dry mixture at T° mm.	695	702	695	697	690
Final pressure of products (in- cluding H_2O) at T° mm.	695	716	722	780	836
Partial pressures (mm.) in original mixture at 0° — C_2H_6	162.3	162.5	162.5	162.5	161.2
O_2	167.7	168.0	168.0	168.0	166.8
Partial pressures (mm.) of gaseous products at 0° — CO_2	0.1	1.9	3.1	9.5	20.2
CO	1.2	12.0	23.0	59.0	99.6
C_2H_6	161.0	149.3	139.2	107.8	80.6
H_2	Nil	Nil	6.0	5.8	5.2
O_2	167.0	160.3	132.3	69.2	1.4
Partial pressures of aldehydes and peroxide reduced to 0° — $CH_3 \cdot CHO$	Nil	1.4	1.9	2.3	Nil
$H_2 : C : O$	Nil	4.2	5.5	6.7	4.3
$C_2H_5O_2$	Nil	0.2	0.5	1.0	Nil
Ratio O_2/C_2H_6 actually used up	0.6	1.25	1.45	1.8	1.85
Units in original mixture	C_2H_6 487 168	C_2H_6 487 168	C_2H_6 487 168	C_2H_6 487 168	C_2H_6 487 168
Units in above products	O_2 325 483 167	O_2 325 483 167	O_2 325 483 167	O_2 325 483 167	O_2 325 483 167
Difference = units as H_2O and "Oxy- C_2H_6 "	323 483 167	320 455 161	315 434 151	297 343 113	285 252 73
	Nil	5 32 7	10 53 17	28 144 55	38 232 94

the formation of peracetic acid and diacetyl-peroxide when either gaseous, liquid or dissolved acetaldehyde is exposed to the action of oxygen in ultra-violet light. Indeed our evidence points to the acetaldehyde stage of the combustion being far the most favourable to "peroxidation." In this connection, there are sound reasons for supposing that, under our experimental conditions, while the further oxidation of gaseous acetaldehyde would normally



would have a "peroxide" reaction, and presumably cause "knock" in explosive combustion.

Signs were wanting in our experiments of any hypothetical primary ethane-peroxide (i.e. $\text{C}_2\text{H}_6\text{O}_2$) formation during the "induction period"; and in this connection it seems possible that what was thought to be peroxide formation by M. Brunner and E. K. Rideal* during their observations upon a similar "induction period" in the interaction of a 42/58 hexane-oxygen mixture at 210°C . may have been caused by aldehyde, especially as they used an acid solution of potassium iodide for its detection.

It may also be noted that these experiments have again confirmed, what has been repeatedly shown before, that the slow non-explosive combustion of ethane proceeds without any separation of carbon or liberation of hydrogen, except in so far as small amounts of the latter may possibly arise adventitiously from the thermal decomposition of formaldehyde which in favourable circumstances may accumulate in the system. Small amounts of methane might similarly arise from the thermal decomposition of acetaldehyde. Neither is ethylene produced, save perhaps in quite negligible proportion presumably by the secondary decomposition of ethyl alcohol.

An inspection of the tables and curves will show that definite proof was forthcoming of the early formation of acetaldehyde, with concomitant smaller amounts of "peroxide," of formaldehyde which presumably followed and certainly survived the acetaldehyde, and in some cases subsequently of formic acid also. Needless to say, the sequence ethane $\rightarrow$ acetaldehyde $\rightarrow$ formalde-

* 'J. Chem. Soc.,' p. 2824 (1928).

hyde $\rightarrow$ formic acid, etc., accords with the "hydroxylation" theory, with allowance of some possible "peroxidation" of C_2H_4O at the acetaldehyde stage.

Unfortunately, save in so far as it discounts "peroxidation," the evidence is less definite than could be wished as to the character of the *initial* stage of the oxidation, although something may be inferred therefrom. This is chiefly due to the insensitiveness (already explained) of present methods for detecting ethyl alcohol among other products (*e.g.*, acetaldehyde) also giving the iodoform reaction, a circumstance which drives us back to such indirect evidence as can be derived from the carbon-hydrogen-oxygen balances of the experiment (*q.v.*).

While admittedly such indirect evidence must be taken with some reserve, because of the balances in question having to bear the brunt of analytical errors, it does (we think) point quite consistently in one direction only, namely, that the initial product is probably an "oxy-ethane" (we advisedly use this term provisionally as being sufficiently non-committal) which, if not ethyl alcohol, C_2H_6O , is less oxygenated than it.

In all but the first one or two experiments of each series, when reaction had scarcely begun, these balances show consistently that, after deduction in each case from the carbon-hydrogen-oxygen units present in the original mixture the corresponding units represented by the various gaseous products *plus* aldehydes, peroxide and formic acid, there remained a balance, not only of H_2 and O_2 units, usually in nearly a 3 : 1 ratio, but usually also of C-units as well. And while the former was largely, but could not wholly be, due to condensed steam from the combustion, the latter must be ascribed to its being accompanied by some soluble or condensable organic oxygenated compound other than those (aldehydes, peroxide, formic acid) already enumerated. And it will be seen that, as might be expected, in both series of experiments such organic compound accumulated in the system as the ratio of oxygen/ethane present diminished.

Now it is clear that ratios consisting of $x C \cdot 3 H_2 \cdot O_2$ (or thereabouts) in these balances can hardly be attributed to admixtures of small proportions of a $C_2H_6O_2$ with H_2O . In two cases they would be perfectly satisfied, and in two others fairly well so, by the supposition of a mixture of C_2H_6O (ethyl alcohol) and H_2O : but in the other four cases they would seem to require an even less oxygenated-ethane than ethyl alcohol. Therefore, so far as it goes, this part of the evidence points to the presence of either C_2H_6O or some less oxygenated-ethane among the soluble and condensable products; and it may be added that calculation has shown that, even had it been wholly C_2H_6O , the amount would

have been insufficient for detection in the rinsings by the iodoform reaction in the presence of aldehydes.

There is, however, further indirect evidence from our experiments supporting the view that ethyl alcohol (C_2H_5O) or some lower "oxy-ethane" rather than $C_2H_5O_2$ is primarily formed in the slow combustion of ethane, namely, that the $2C_2H_6 + O_2$ is so much more reactive than the $C_2H_6 + O_2$ mixture. And this, combined with the abundant formation of ethyl alcohol (followed by that of acetaldehyde and acetic acid) when ethane is oxidised by ozone at $100^\circ C.$, may be regarded as sufficiently good grounds for our continuing to hold the "hydroxylation" view of the initial oxidation stage while not relaxing our efforts eventually to isolate and identify the prime product.

(6) *Carbon-Hydrogen-Oxygen Balances for a $C_2H_6 + 2O_2$ Mixture at $323^\circ C.$*

Finally, as a check upon the procedure adopted in regard to the carbon-hydrogen-oxygen balances in the foregoing experiments, a special experiment was carried out in which a mixture originally containing $C_2H_6 + 2O_2$ was introduced into the reaction vessel at 690 mm. pressure ("dry" and N_2 -free and $T = 323^\circ C.$). After an induction period of 25 minutes, during which there was no change, the pressure rose during the next 23 hours to 850 mm., when reaction ceased. The vessel and its contents were then suddenly cooled to $0^\circ C.$ by plunging them into an ice-water mixture, and a sample of the products was removed for analysis. The reaction vessel was finally rinsed out with 20 c.c. of water, but when tested the rinsings were perfectly neutral and showed no signs whatever of the presence of either "peroxide" or acetaldehyde; with Schiff's reagent they gave the faintest possible sign of reaction after an hour, which indicated possibly the presence of a trace of formaldehyde. The partial pressures of the ethane and oxygen in the original mixture and of the various gaseous products were as follows:—

	Equivalent to units of		
	C.	H ₂ .	O ₂ .
Partial pressures in original mixture at 0° C.—			
C ₂ H ₆ = 108.8 mm.	217.6	326.4	211.2
O ₂ = 211.2 „			
Partial pressures in gaseous products at 0° C.—			
CO ₂ = 55.5 mm.	217.0	104.6	103.4
CO = 94.3 „			
C ₂ H ₆ = 33.6 „			
H ₂ = 3.8 „			
O ₂ = 0.8 „			
Balance (H ₂ O) =	0.6	221.8	107.8

$$\text{Ratio } \frac{221.8}{107.8} = 2.06.$$

It will be seen that all but 0.3 per cent. of the original carbon was thus accounted for and that the ratio of the unaccounted for H₂ and O₂ was 2.06 or practically as required for condensed steam.

Summary.

The principal points concerning the slow homogeneous interaction of ethane and oxygen mixtures at *circa* 300° C. and atmospheric pressure brought out by the experiments described in this paper may be summarised as follows, namely :

- (i) The interaction has the characteristics associated with "chain reactions," and is preceded by a well-marked "induction period" during which practically no oxidation occurs, the gases (or one of them) merely "getting ready" in some way.
- (ii) The induction period is either shortened or obliterated altogether by the addition of small amounts (*e.g.*, 1 per cent.) of moisture, ethyl alcohol, formaldehyde, iodine, nitrogen peroxide, etc., to a dry C₂H₆ + O₂ medium without altering the non-explosive character of the ensuing combustion; an addition of 1 per cent. of acetaldehyde vapour, however, causes an instantaneous inflammation of the medium.
- (iii) Both the "induction" and the "reaction" periods are much shorter for a 2C₂H₆ + O₂ than for a C₂H₆ + O₂ mixture in the circumstances referred to; and an increase in oxygen content beyond an equimolecular proportion rapidly lengthens both of them. Thus the general "reactivity" of ethane-oxygen mixtures in such circumstances is largely

determined by the relative ethane concentration, a conclusion which is entirely in line with that reached by H. W. Thompson and C. N. Hinshelwood in their work on the kinetics of the oxidation of ethylene (*loc. cit.*).

- (iv) Such slow combustion proceeds quietly, as previously shown by Bone and Stockings (*loc. cit.*), without any separation of carbon or liberation of hydrogen, in a manner consistent with the "hydroxylation" view, *via* the intermediate formation of acetaldehyde, formaldehyde, formic acid and probably carbonic acid to the ultimate production of oxide of carbon and steam.
- (v) Although inconsiderable amounts of a "peroxide" are, or may be, formed as a concomitant of the acetaldehyde, pointing to the possibility of "peroxidation" of C_2H_4O at the acetaldehyde stage, no evidence was forthcoming of any earlier "peroxide" formation, as for instance a primary $C_2H_6O_2$ formation. Accordingly peroxidation and immediately formed aldehydes, rather than initials of the hydrocarbon, would seem to be the more probable cause of "knock" in petrol-air explosions.
- (vi) Although ethyl alcohol was never actually identified among the soluble or condensable oxidation products, there were grounds for believing that either C_2H_6O or some less oxygenated-ethane was present as the initial product.

In further experiments we propose investigating more fully such matters as (1) the nature of the "induction period"; (2) the influences of third bodies generally, and particularly of acetaldehyde and formaldehyde, thereon, as well as their influences in quickening the subsequent combustion; (3) the slow combustion of both ethyl alcohol and acetaldehyde, particularly with a view to elucidating further the problem of "peroxidation" during the latter; and (4) we are continuing unabated our efforts more definitely to identify, and if possible isolate, the primary oxidation product.

In conclusion, we desire to express our thanks to the Gas Light and Coke Company of London for the Research Fellowship, the tenure of which has enabled one of us to devote his whole time to the work.

*Absolute Intensity of the Aurora Line in the Night Sky, and
the number of Atomic Transitions Required to Maintain it.*

By Lord RAYLEIGH, For. Sec. R.S.

(Received September 9, 1930.)

Some time ago Prof. S. Chapman, F.R.S., pressed upon me the importance of making an absolute determination of the intensity of the auroral green line in the night sky, in order to fix the number of atomic transitions per second required to maintain it. Such a determination will be of value even if not of high accuracy. Indeed, as I have shown in previous papers, the intensity is itself variable over fairly wide limits: so that in any general statement of the absolute value, high accuracy is out of the question.

The difficulty of the problem arises from the faintness of the light of the auroral line, and the fact that it is not isolated but superposed on a background of apparently continuous spectrum, from which it cannot in the nature of the case be completely separated without the use of high spectroscopic resolving power. The last usually involves loss of light and restriction of the angular size of the photometric field. There is too little light to begin with to allow of this.

Some years ago I described what I call an "auroral filter,"* which isolates the green line as closely as may be with the minimum loss of light, and, of course, without restriction of the angular field of view. The filter consists of Wratten No. 21 gelatine filter combined with dense didymium glass. This combination used on the night sky cuts out all but a band of an ill-defined width, which may be put at about 200 Ångström around the green auroral line λ 5577. It is true that some red light of wave-length 6000 Å upwards is transmitted, and when a bright source is examined (*e.g.*, the day sky) this seems at first glance to make the action of the filter altogether unsatisfactory. The objection disappears, however, on closer examination, because the dark adapted eye is insensitive to the red light transmitted. This is readily demonstrated by examining the night sky through a red filter, Wratten No. 26. Though this transmits more red light than the auroral filter, it is apparently as opaque as a piece of metal to the night sky. We conclude that *on the night sky* the red transmission of the auroral filter is a blemish of no importance.

* 'Proc. Roy. Soc.,' A, vol. 106, p. 119 (1924).

The filter was found* to transmit $1/2.5$ of the green line of krypton at λ 5570. This was taken with sufficient accuracy to be also the transmission of the aurora line at λ 5577.

The light passing the auroral filter will in the first instance be taken to consist entirely of the green line. In this way an upper limit to the luminous intensity will be obtained. An attempt will then be made to estimate the deduction to be made for the fact that some light belonging to the continuous background of the spectrum is transmitted.

In the present work I have not made any direct observation on the sky. The problem has been limited to calibrating absolutely the scale of intensities in the long series of observations that have been made on the sky for seven years past; in other words, the absolute intensity of auroral light required to match the self luminous working standard of potassium-uranyl sulphate† has been determined. For this purpose, an approximately mono-chromatic source of wave-length near λ 5577 must be set up, of which the absolute energy per unit solid angle is known in ergs per second. The practical difficulties of doing this are at first sight not inconsiderable, but a solution has been found which is thought fairly satisfactory.

It was at first contemplated to standardise such a source by bolometric methods, but the more this was considered the more difficult did it appear, especially since my laboratory had been destroyed by fire‡ and I had to work, if at all, in extemporised quarters.

I have therefore made use of heterochromatic photometry, which, though a disagreeable kind of measurement to carry out, gives a result sufficiently trustworthy.§ The photometric result can be translated into energy by the known "mechanical equivalent of light" for the wave-length in question. In this work the eye has been used as an instrument of comparison in two different conditions:—

- (1) In full light.
- (2) Completely dark adapted.

The reader must be reminded that the relative intensities of two lights of different wave-lengths are *totally different* according to which condition the

* *Loc. cit.*

† Maintained by its own radioactivity. See 'Proc. Roy. Soc.,' *loc. cit.*, p. 121.

‡ March 6, 1930.

§ On heterochromatic photometry, see 'Photometry,' by J. W. T. Walsh (pub. Constable), 1926, chapter VIII. This book has been of much assistance throughout the present investigation.

eye is in (Purkinje effect). In intermediate conditions of the eye, there is nothing definite about this intensity ratio. But in either of these two limiting conditions a normal eye, the ratio is definite, and can be arrived at independently by different observers.

In designing the mono-chromatic source, easily maintained constancy is one of the most important considerations. This tends to rule out bright line sources such as a krypton vacuum tube. A moderate range of wave-length around the desired value is permissible, provided that the light does not differ sensibly in its mean "mechanical equivalent" from $\lambda 5577$. Fortunately the mechanical equivalent is at a minimum in this neighbourhood, which makes the condition easy to meet. An incandescent lamp run under standard conditions and filtered through the auroral filter, fulfils most of the requirements, but to make it quite suitable it is necessary to supplement this filter by a green glass, which cuts out the red transmission already mentioned. This red transmission which, as already explained, is of no importance when the dark adapted eye is concerned, is inadmissible when the light behind is bright, and vision is normal. It is, therefore, necessary to use the green glass which removes it.*

It is necessary to determine in what ratio the candle-power of the standard lamp is cut down by the use of this filter, which we may call the "supplemented auroral filter." It is here that heterochromatic photometry under full illumination becomes necessary. As is known, the flicker method gives the most accurate results, but the means of adopting it were not available. The light of the standard lamp was made to yield a bright field by means of a suitable field lens, which latter was of quartz, so that it introduced no colour of its own.† For comparing this bright field, as seen with and without the filter, I used the comparison photometer formerly described.‡ The field as viewed through the supplemental auroral filter was matched by a comparison

* This is neither necessary nor admissible in the normal use of the filter on the night sky, because of the serious loss of green auroral light incidental to filtering out the red light.

† In order to make sure that the brightness was ample to bring the eye into the limiting condition, a 30-watt opal bulb gas-filled lamp was sometimes used to give the bright field, being run at a voltage determined to give an exact colour match with the standard lamp. The latter (not being gas filled) was designed to run at a lower colour temperature than the opal lamp. The colour match was made on a Lummer-Brodhun photometer head, and the opal lamp, rated at 110 volts, was run at 86 volts. The bulb itself afforded the bright field without the use of a lens. It was brought close up. The results with this brighter field were not sensibly different from those obtained directly with the standard lamp and quartz lens.

‡ 'Proc. Roy. Soc.,' *loc. cit.*, pp. 126, 129.

field reduced by a calibrated series of neutral glasses proceeding by unit steps on my scale, which are equivalent to 0.1 H. and D. An additional neutral glass, movable from side to side, allowed the balance to be readily thrown over, so as to secure equality of contrast in the two positions. This does in effect what is done by moving the photometer head to and fro on a photometer bench.

In order to avoid bias and to determine to what extent the judgments of an individual observer were definite and reproducible, the neutral glasses were arbitrarily changed to and fro by an assistant, without the observer's knowledge, and he was required to say whether the neutral field was brighter or darker than the green one. His verdicts were recorded without comment. By making a number of settings, usually about 25, in the neighbourhood of equality, the observer's mean judgment for that day could be determined. By tabulating the verdicts that particular setting (if any) could be selected for which the observer judged the neutral field to be *darker* as often as he judged it *brighter*. If no setting exactly corresponded to this result, an interpolation was made to arrive at it. The more successful observers did not often give judgments which differed by more than ± 1 from the final mean of the set of 25.

A number of observers were called in, so as to avoid personal peculiarities as far as possible. The younger observers (ages 15 to 18) were on the whole less successful than older ones. Those who gave their judgments with least hesitation were found most consistent with themselves and with the general mean. In some cases where observers were inexperienced and results anomalous, a new series was taken on another day, without giving any clue to what was expected. This always produced a nearer approach to the general mean, due no doubt to practice in the comparison. In all cases the *last* day's result is taken which seems a reasonably impartial method.

The results were as follows :—

Observer.	Age.	Sex.	Result.
R.	54	Male	18.9
R. T.	38	Male	18.8
G. I. C.	18	Male	17.0
H. V. S.	15	Male	18.2
D. S.	18	Female	17.0
H. D. C.	20	Male	19.5
J. A. S.	22	Male	19.0
V. C.	19	Female	18.5

The mean is 18.4, representing a factor of 69.2. It is hoped that this factor is correct within about ± 10 per cent., but even if it were in error ± 20 per cent. this would not be of much importance for the purpose in hand.

The candle-power of the lamp run at the standard voltage and in the relevant direction was determined at the National Physical Laboratory as 0.735 international candles. Thus its candle-power through the supplemented auroral filter is $0.735/69.2$ or 0.0106 candles.

To diffuse the light of this source, a screen covered with magnesium oxide (smoke of burning magnesium) was used. The screen was set up so that the light fell normally upon it.

The magnesium oxide screen was observed at an angle of 30° to the normal, and the distance of the light was adjusted till this was a match for the self luminous source in the night sky photometer. In this observation the illuminated screen was observed in just the same way that the sky is observed in the ordinary use of the instrument *with the dark adapted eye*. The intensity of the self luminous source is indeed so low as automatically to secure this condition of the eye. The logic of this procedure must be carefully observed. The auroral light of the sky is in the ordinary use of the instrument equated to the self luminous source. The quasi-auroral illumination of the magnesia screen is also equated to the source, using the same arbitrary criterion of equality as before, namely, what appears such to the dark adapted eye. We can then eliminate the self luminous source, and equate the auroral light of the sky to the quasi-auroral light of the illuminated screen. As these two latter are approximately of the same kind their equality may be treated as absolute, independently of the particular detecting instrument that is used. They have, therefore, the same specific energy emission.

The standard instrument labelled No. 0, which defined the scale adopted in my papers on the light of the night sky, gave equality at a distance of 31 feet or 9.45 metres. The illumination of the magnesia screen under these conditions is $0.0106/(9.45)^2$ or 1.18×10^{-4} metre-candles.

If the surface acted as a perfect diffuser, *i.e.*, one obeying Lambert's law of the cosine, and if its reflexion-factor were 100, then its brightness would be

$$1.18 \times 10^{-4} / \pi \text{ candles per square metre.}$$

In our case of a magnesia surface, illuminated normally, and viewed at 30° from the normal the brightness is 0.92 of this,*

$$\frac{0.92}{\pi} \times 1.18 \times 10^{-4},$$

or 3.46×10^{-5} candles per square metre.

* See Walsh's 'Photometry,' pp. 114, 476. The properties of an ideal diffuser introduced into this mode of statement, do not really enter into the matter. We only use the experimental fact that a magnesia surface illuminated normally by 1 metre-candle has a

The intensity of the sky as seen through the auroral filter varies considerably, and the variations have been under investigation since 1923.* It is not proposed to go into the question here. If the sky as seen through the filter matches the source, the auroral intensity is recorded as 0 on my scale. For simplicity this will be taken as a typical value. It is true that the typical value was taken as $+0.8$ (*loc. cit.*, p. 21). This refers to observations taken near the pole. I have seldom observed at the zenith, owing to the fact that the observations were made out of a window. Assuming this to be somewhat fainter, 0.0 may be taken as a representative value for the zenith, and also gives the calibration of the instrument.

We take it then that the brightness of the zenith sky as seen through the auroral filter is typically

$$3.46 \times 10^{-5} \text{ candles per square metre.}$$

The auroral filter cuts down the light of the krypton line 5570, and (it is assumed) that of the aurora line 5577 also, by the factor 2.5. Allowing for this the actual brightness would become $2.5 \times 3.46 \times 10^{-6}$

or

$$8.65 \times 10^{-5} \text{ candles per square metre.}$$

This, it must be repeated, is on the hypothesis that the auroral filter transmits the green line only, uncontaminated by the background of the spectrum. As there certainly is some contamination, it only gives in reality an upper limit to the intensity.

It remains to determine what fraction of the light transmitted by the auroral filter is really light of the auroral line. This, it must be confessed, is the least satisfactory part of the investigation.

We do not know anything *a priori* about the nature of the approximately continuous spectrum on which the line is superposed. The most obvious supposition—that it is identical with the light of the day sky, has been proved quite incorrect† for the ratio of blue to red is much lower than for the day sky. In the absence of such knowledge of the continuous spectrum the only completely satisfactory method would be to make use of a spectroscopic resolving power sufficient to separate the line from the continuous spectrum in a way brightness of 0.292 candles per square metre in a direction 30° from the normal. For comparison with the properties of a perfect diffuser the factor 0.292 may be written $0.92/\pi$.

* See 'Proc. Roy. Soc.,' A, vol. 119, p. 11 (1928). The work is still in progress.

† See 'Proc. Roy. Soc.,' A, vol. 103, pp. 133-4 (1924); also Dufay, 'J. Physique,' vol. 10, p. 219 (1929), who has come to the same conclusion.

that may be considered virtually complete. But this involves the difficulties inherent in visually observing a faint light when the field of view is narrow, as in a spectrum line. The auroral filter was indeed originally designed to turn these difficulties by giving approximate isolation of green auroral light with a wide field of view.

To get some basis for making an estimate of how much of the light transmitted by the auroral filter is due to continuous spectrum, I have matched the ratio red/blue of the night sky by means of a suitably selected source of continuous spectrum.

This source, when adjusted to give the same actual intensity as the night sky through the blue and red filters, gives a less intensity through the auroral filter. This less intensity is assumed to represent what the night sky *would* give if the light of the green line were abstracted, leaving out the continuous light transmitted by the (unavoidably imperfect) auroral filter.

The reader must form his own estimate of how this procedure is plausible. The basic supposition of course is that the continuous spectrum of the sky, matched at the blue and the red parts of the spectrum by an incandescent source, will also be matched in the yellow-green. It is in effect a method of estimating the yellow-green intensity, by interpolation between the parts of the spectrum on either side.

The source which was found most suitable for imitating the blue/red ratio of the night sky was a pointolite lamp (enclosed tungsten arc). This was diffused by a magnesium oxide screen and a crude image of this screen was formed on a similar screen in another room by a hole 3 cm. in diameter in the intervening partition wall. The intensity could be regulated by the distance of the lamp from the first screen. The second screen was thus brought to an intensity comparable with the night sky, though, for convenience, somewhat greater.*

Observing the screen thus illuminated through the red filter Wratten 23A and the blue-green Wratten 65A, it was found that these could be matched by placing a neutral glass No. 7 on my scale (0.7 H. and D.) over the blue-green. The filters were held in the comparison instrument already referred to.

Similarly, the auroral and red filters could be matched for intensity by putting neutral glass No. 1 over the former.

I express this shortly by writing

$$\text{Blue-red} = 7,$$

$$\text{Auroral-red} = 1,$$

* The illumination could of course, be reduced to the desired point with only one screen, if the source were far enough off. Inconveniently long distances would then be necessary.

but it must be remembered that the scale of neutral glasses ascend by equal increments of *density* not of *opacity*.

My records include a large number of cases for which the relation Blue-red = 7 holds good for the night sky. Under these circumstances the difference auroral-red has, on different occasions, taken every value between 1 and 5 inclusive. These extreme values are rare, however. The intermediate value
auroral-red = 3
is the most frequent.

According to the method of interpretation proposed, this indicates that the intensity of the line $\lambda 5577$ varies very much relative to that of its continuous background. I had already inferred this from the fact that the intensity as observed through the auroral filter is not an absolutely infallible guide as to whether the green line will be discernible in the spectroscope.*

The following table gives the numerical interpretation :—

	Auroral-red. Neutral glass No.	Auroral filter.		
		Total transmission —background. Neutral glass No.	Intensity ratio r total background.	$1 - 1/r$ (line intensity) = (total intensity).
Lowest	1	0	1.00	0.0
Most frequent	3	2	1.58	0.37
Highest	5	4	2.51	0.60

We shall take the most common case, when, as the table shows, the intensity of the line 5577 is reckoned as 0.37 of the total intensity transmitted by the auroral filter.†

The brightness of $\lambda 5577$ thus becomes $0.37 \times 8.65 \times 10^{-5}$
or

$$3.2 \times 10^{-5} \text{ candles per square metre.}$$

* See Gerlands 'Boiträge zur Geophysik,' vol. 19, p. 295 (1928).

† On this assumption we can estimate what fraction of the total light of the night sky consists of $\lambda 5577$, assuming comparison to be made by the dark-adapted eye. The total light is often reduced 13.4 times by the filter, and the green krypton line, taken as equivalent to 5577, is reduced 2.5 times (Proc. Roy. Soc., A, vol. 103, p. 120 (1923)). If the light transmitted by the filter were pure $\lambda 5577$, the proportion of the latter would be $2.5/13.4 = 0.187$. Introducing the factor 0.37 above arrived at we get $0.37 \times 0.187 = 0.069$ as the fraction of the whole light consisting of $\lambda 5577$. This is in substantial agreement with the results of Dufay, *loc. cit.*, p. 228. He finds 0.089 to 0.060. The methods are entirely different. In this case we are comparing intensities as seen by the dark-adapted eye.

The emission from the atmospheric layer differs essentially from the emission by an ideal diffusing surface. The latter is uniformly bright in front from whatever direction it is viewed, but it emits no light from behind. The luminous atmospheric layer emits light from both sides, and the brightness is presumably greater in an oblique direction. Each element of volume may be considered to act independently, and we ought to get increased brightness by looking through a thicker layer, as in the case of an end-on vacuum tube used in laboratory spectroscopy. This should lead to increased brightness of the night sky near the horizon, and such an effect is at times conspicuous. More often it is not so, being presumably obscured by poor atmospheric transparency. I hope to investigate this matter carefully later on. It is assumed here that whereas a diffusing surface having a brightness B candles per square metre emits πB lumens per square metre, the sky layer emits $4\pi B$ lumens per square metre. In fact, each element of volume acts like a spherically uniform source having the same candle power in all directions. If there were any appreciable complication due to absorption and re-emission of λ 5577, this would not be justified. The line, however, is not a resonance line and cannot be absorbed by oxygen in its ordinary state. Although present in the solar spectrum in absorption* it is not enhanced when the sun is low, and atmospheric absorption is at its maximum. We have, therefore, no reason from any point of view to think that absorption and re-emission occur to any important extent in the earth's atmosphere.

We conclude then that the total emission amounts to $4\pi \times 3.2 \times 10^{-5}$

or

$$4.02 \times 10^{-4} \text{ lumens per square metre.}$$

To turn this into energy, we make use of the "mechanical equivalent of light." This is usually given for the wave-length λ 5560, which corresponds to maximum luminosity in the spectrum, and therefore minimum mechanical equivalent. The value adopted is 0.0016 watts per lumen.† The wave-length λ 5577 with which we are concerned is so near the minimum at λ 5560 that the variation of mechanical equivalent is not worth considering. The energy of emission of λ 5577 from the night sky then becomes $4.02 \times 10^{-4} \times 0.0016$

or

$$6.4 \times 10^{-7} \text{ watts per square metre}$$

or

$$6.4 \text{ ergs. per second per square metre.}$$

* Sommer, 'Z. Physik,' vol. 58, p. 575 (1929).

† Walsh, 'Photometry,' p. 297.

The energy of 1 atomic transition of wave-length λ 5577 is 2.22 electron-volts or 3.53×10^{-12} ergs. Thus 6.4 ergs. represents 1.81×10^{12} transitions, and the energy of emission of λ 5577 from the zenith sky, when its intensity has that ordinary value which corresponds to 0 on the scale of the standard instrument, requires for its maintenance

1.81×10^{12} atomic transitions per square metre per second.

Summary.

In this work the standard instrument used in measuring the green auroral light of the night sky is calibrated. The instrument uses a special filter designed to isolate the green auroral line as nearly as possible. If the transmitted light is assumed to consist entirely of λ 5577, the brightness corresponding to the zero reading of the instrument is found to be

8.65×10^{-5} candles per square metre,

which is an upper limit to the brightness of λ 5577 in any source which gives this zero reading.

In fact, the light transmitted by the filter consists in part of the green line, and, in part, of continuous background. The fraction attributable to the former is variable; its most common value is estimated at 0.37.

The brightness of the line then becomes

3.2×10^{-5} candles per square metre.

This is the zero reading of the standard photometer, but (as it happens) also corresponds very closely with the mean observed brightness on the night sky, corrected to the zenith.

The energy required to maintain it is

6.4 ergs. per second per square metre,

and the number of atomic transitions required to supply this energy is

1.81×10^{12} per second per square metre.

The Structure of Synthetic Mixed Triglycerides.

By RAMKANTA BHATTACHARYA and THOMAS PERCY HILDITCH, Department of Industrial Chemistry, University of Liverpool.

(Communicated by E. F. Armstrong, F.R.S.—Received June 30, 1930.)

A study has been made of the distribution of saturated and unsaturated fatty acids in triglycerides produced synthetically by esterification of selected mixtures of saturated and unsaturated higher fatty acids with glycerol, in order to compare the general structure of these synthetic products with that of a number of natural fats.

The component glycerides of many natural fats have recently been investigated in these laboratories, by converting all unsaturated groupings into acidic products by oxidation of the glycerides with anhydrous potassium permanganate in acetone solution; only fully-saturated triglycerides present in the original fat are then left in the form of neutral compounds. This mode of attack leads primarily to a quantitative statement of the relative distribution of saturated and unsaturated acids in the glyceride molecules of a fat, but, if the combined fatty acids in the whole fat and in the fully-saturated portion are analysed in detail, and if oleic and linoleic acids (as is frequently the case) are the only unsaturated derivatives present, additional information as to the relative distribution of individual fatty acids can frequently be given. The general results of the observations on natural fats have been summed up in a recent communication* in which it was shown that the glyceride structure varies with the biological type of the fat. In vegetable seed fats there is a pronounced tendency to even distribution of fatty acids throughout the glycerides; an acid (*e.g.*, oleic acid), when present in subordinate amounts, tends to become linked with about 1·3 to 1·5 molecules of an acid which is present in larger proportions and, in consequence, as between saturated and unsaturated groups, the amount of fully-saturated glyceride present in a seed fat is, broadly, determined by the amount linked with unsaturated acids in the above favoured ratio. Thus in seed fats fully-saturated glycerides do not appear in appreciable quantity until the molecular proportion of saturated fatty acids in the total fatty acid mixture reaches about 60 per cent. In contrast to seed fats, the glycerides of vegetable pericarp fats and of animal fats such as various depot fats and milk fats are constituted on more heterogeneous lines, albeit in a

* Collin and Hilditch, 'Biochem. J.', vol. 23, p. 1273 (1929).

manner which at first sight is more akin to that which would be anticipated if the laws ordinarily operative in esterification were followed.

Mixtures of specific saturated fatty acids and unsaturated fatty acids have now been esterified with glycerol in such a way that triglycerides were obtained and the distribution of saturated and unsaturated acids in the synthetic triglyceride molecules has then been studied by the permanganate acetone oxidation process. Much work has, of course, already been devoted to the synthesis of triglycerides of definite structure by the application of more or less involved procedure. The problem before us was, however, not the preparation of glycerides of particular configuration, but the determination of the manner in which saturated and unsaturated fatty acids divide themselves amongst molecules of glycerol when esterification is allowed to proceed in the laboratory under the simplest conditions possible.

It has long been known that glyceride formation is effected smoothly by merely heating glycerol and higher fatty acids together at an appropriate temperature, reduction of pressure being preferably employed to assist the removal of water from the sphere of interaction; it is further obvious that complete esterification of the glycerol (*i.e.*, complete formation of triglycerides) will be promoted by the presence of an excess of the fatty acid mixture, whilst it has also been known for a considerable time that esterification of higher fatty acids with glycerol is accelerated by the presence of small quantities of aromatic sulphonic acids. In the preparation of triglycerides for the purpose of this study the fatty acid mixture (about 110 g.) was heated with 80 to 90 per cent. of the theoretical quantity of pure glycerol and 0.5 per cent. of naphthalene- β -sulphonic acid at 135 to 145° for 5 to 6 hours in a vacuum of about 1 mm.; under these conditions it was found that the whole of the glycerol retained in the product was in the form of triglycerides, but that in the absence of the sulphonic acid catalyst a considerably higher temperature was required. It was felt that the presence of this minute proportion of catalyst was preferable to the use of higher temperatures.

Comparatively large quantities of unsaturated acids were required and, in view of the tedious and somewhat costly procedure requisite to yield the necessary amount of pure oleic acid, it was decided to use the unsaturated acids (a mixture of about 85 per cent. oleic and 15 per cent. linoleic acid) from olive oil, prepared by removal of saturated fatty acids as lead salts. The iodine absorption of these unsaturated acids was 104 per cent., equivalent to 99.1 per cent. for the corresponding glycerides.

Lauric and palmitic acids were obtained from carefully fractionated specimens

of their methyl esters, and stearic acid from methyl stearate prepared by hydrogenation of methyl oleate; the palmitic and stearic acids employed still contained respectively 4 per cent. and 9 per cent. of oleic acid, this being allowed for in making up the mixtures of saturated and unsaturated acids for conversion into triglycerides.

Absence of mono- or di-glycerides from the synthetic triglycerides was verified by determination of the saponification equivalent of each product, whilst the actual proportion of saturated and unsaturated acids in the synthetic glycerides was estimated from the iodine absorption of the latter, since in some cases (*v. infra*) the saturated and unsaturated acids were found to possess different rates of esterification, so that the proportions combined in the glycerides were not in these instances quite the same as in the original mixture of acids.

The purified triglycerides (ca. 50-100 g.) were oxidised in acetone solution (10 volumes) by carefully adding four times their weight of powdered potassium permanganate at such a rate as to maintain a fairly rapid action and constant ebullition of the acetone throughout the process, and the unchanged fully-saturated glycerides were recovered according to the procedure which has been given in detail elsewhere. In stearic-oleic mixtures and a few palmitic-oleic mixtures, it was found preferable to remove most of the tristearin (or tripalmitin) by crystallisation of the synthetic glycerides from ether and to conduct the oxidation only on the ether-soluble portion; when this course was followed it was necessary to continue the recrystallisation of the synthetic material until the separated portion possessed a negligible iodine absorption.

In cases where the proportion of unsaturated glycerides was 50 per cent. or less of the synthetic fat, one oxidation was in general sufficient; but with materials of greater degree of unsaturation the initial product obtained by oxidation still contained unsaturated compounds and it was necessary to repeat the oxidation process a second time.

Synthetic Triglycerides Studied.

In Table I are collected the data for the triglycerides synthesised as described, including the molecular proportions of saturated and unsaturated acids in the mixtures submitted to esterification, the observed iodine absorption of the synthetic product, and the corresponding molecular proportions of saturated and unsaturated components therein.

Table I.—Composition of Synthetic Glycerides.

Saturated acid.	Fatty acids esterified.		Synthetic triglycerides obtained.		
	Molecules saturated.	Molecules unsaturated.	Iodine absorption (found).	Molecules saturated.	Molecules unsaturated.
	per cent.	per cent.	per cent.	per cent.	per cent.
Lauric	50	50	43.1	64.3	35.7
"	70	30	27.6	78.2	21.8
"	80	20	19.9	84.6	15.4
"	90	10	10.0	92.5	7.5
Palmitic	33	67	68.0	33.5	66.5
"	40	60	61.4	40.2	59.8
"	50	50	51.0	50.8	49.2
"	60	40	40.0	61.8	38.2
"	67	33	35.0	66.8	33.2
"	70	30	33.0	68.7	31.3
"	80	20	22.0	79.4	20.6
"	85	15	15.9	85.2	14.8
"	90	10	10.3	90.4	9.6
Stearic	50	50	43.6	55.9	44.1
"	70	30	27.8	71.8	28.2
"	80	20	18.4	81.4	18.6
"	90	10	8.9	90.9	9.1

It will be observed that in the case of the lauric-unsaturated acid esterifications the acid of lower molecular weight was distinctly more readily esterified and the glycerides contained higher proportions of lauric acid than the original fatty acid mixture. Palmitic and oleic acids, on the other hand, were esterified at about the same rate, the observed composition being in each case close to that of the fatty acid mixture employed. With stearic acid, however, the agreement is not quite so close.

No marked difference in rate of esterification is observable until the difference in molecular size of the saturated and unsaturated acids (*i.e.*, lauric and oleic) becomes considerable.

Proportion of Fully-saturated Glycerides in the Synthetic Fats.

The results of the quantitative oxidations carried out are summarised in Table II, which shows (1) the molecular percentage of saturated acids in the synthetic glyceride; (2) the percentage by weight and also (3) the corresponding molecular proportion of fully-saturated glycerides therein; fig. 1 shows the molecular proportion of fully-saturated glycerides plotted against the molecular percentage of saturated acids present in the whole of the synthetic fats.

Table II.—Fully-saturated Glyceride Content of Synthetic Glycerides.

Saturated acid.	Molecular proportion of saturated acids present.	Fully-saturated glycerides.	
		Weight.	Molecular proportion.
	Per cent.	Per cent.	Per cent.
Lauric	64.3	16.9	20.2
"	78.2	39.3	43.9
"	84.6	53.0	57.0
"	92.5	72.8	75.6
Palmitic	33.5	5.1	5.3
"	40.2	7.5	7.9
"	50.8	12.3	12.9
"	61.8	21.1	21.9
"	66.8	23.4	24.2
"	68.7	29.9	30.8
"	79.4	49.9	50.9
"	85.2	57.4	58.2
"	90.4	73.0	73.7
Stearic	55.9	16	16
"	71.8	32	32
"	81.4	50	50
"	90.9	74	74

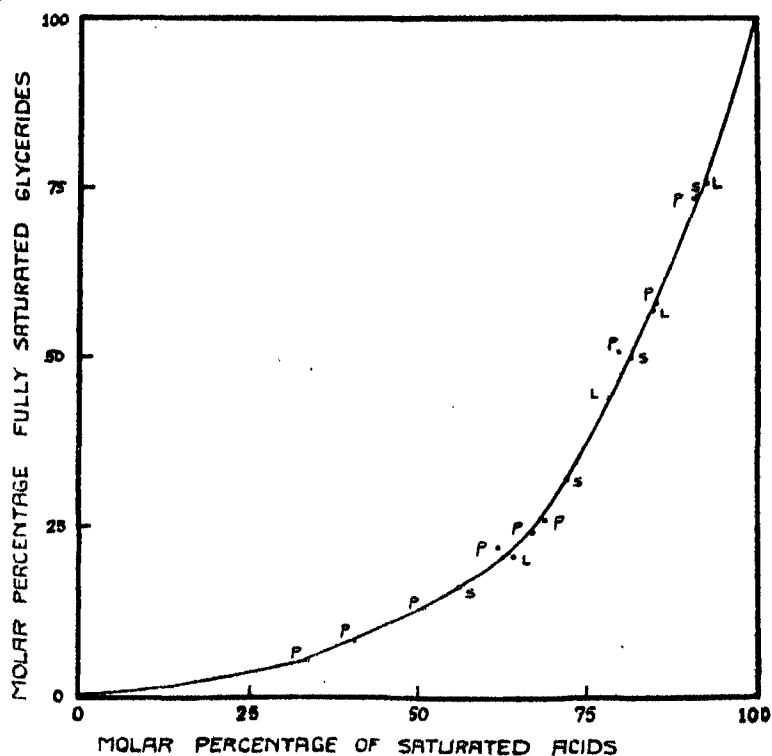


FIG. 1.

All the values obtained lie (within experimental error) on a smooth curve and it may be concluded that mixtures of fatty acids when esterified with glycerol under the conditions applied yield a mixture of triglycerides, the general composition of which is determined by the curve given. The presence of three replaceable hydroxyl groups in glycerol renders the interpretation of the relationships involved complicated and, as a matter of fact, we are at present engaged in investigating the simpler case of the distribution of fatty acid molecules between those of ethylene glycol when higher fatty esters of glycol are similarly prepared. If the chances of fully-saturated triglycerides being produced are calculated on the assumption that fatty acid molecules are selected indiscriminately three at a time according to their relative concentrations, a graph is obtained not very dissimilar in form from the experimental curve in fig. 1, but intersecting the latter at the point corresponding with equimolecular amounts of saturated and unsaturated fatty acids in the synthetic glycerides as a whole; when saturated acids are in excess of the unsaturated acids the observed percentage of fully-saturated glyceride molecules is somewhat less than that calculated as described, whilst the reverse holds for glycerides containing an excess of unsaturated over saturated acids.

It is interesting to compare the observed results for synthetic glycerides with those obtained up to the present in the case of natural fats. These are illustrated in fig. 2, in which the curve is a reproduction of the experimental graph in fig. 1, whilst the dotted line represents the relationship which would hold for glycerides in which the amount of fully-saturated compounds was determined by the association of 1.4 molecules of saturated acid per molecule of unsaturated acid in the form of mixed glycerides. The relevant data for the natural fats are collected in Table III from results obtained by various workers in these laboratories as indicated in the accompanying list of references.

The figures for all the vegetable seed fats given in the first part of Table III correspond with points on the graph which lie either along the horizontal axis or in close proximity to the dotted line in fig. 2. The values for pericarp fats and for animal fats, on the other hand, tend to follow the experimental curve, although they are by no means congruent with it.

In both pericarp fats (*Stillingia* tallow and palm oils) the content of fully-saturated glycerides is rather less, for a given degree of general unsaturation, than in the case of synthetic glycerides, but the trend of the figures as a whole provides a curve approximately parallel with the observed graph. It so happens that the composition of *Stillingia* tallow leads to points on the graph

which are not far removed from the intersection of the synthetic glyceride curve and the linear relationship for fats with association ratio 1.4 : 1 in the

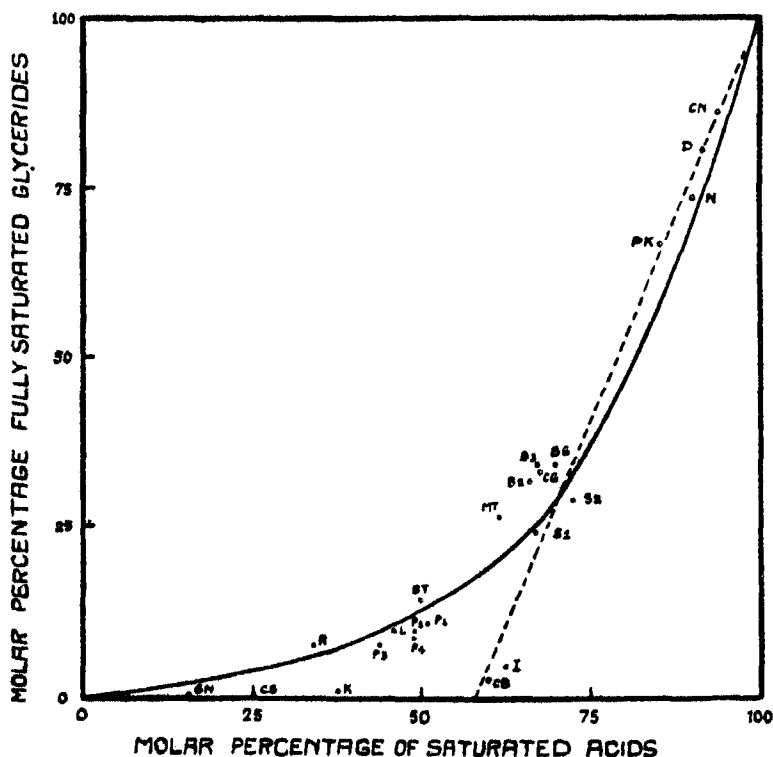


FIG. 2.

mixed glycerides, but taken in conjunction with the palm oil data, both groups of fats show similar relationship to the synthetic glyceride curve.

On the other hand, the data for rabbit fat, beef and mutton tallow and the milk fats form a group, or series of groups, which are mainly parallel to the experimental curve, but in this case on the opposite side from that of the pericarp fats; the value for lard is almost coincident with the curve for the synthetic fats. In other words, in tallows and milk fats the proportion of fully-saturated glycerides for a given mixture of saturated and unsaturated fatty acids in the whole fat tends to be higher than in the case of the esterified glycerides. The results of work at present in progress on a range of milk fats and also on a series of beef tallows may perhaps bring out further group similarities or contrasts; the data for the four palm oils already form a group of this kind quite consistent amongst themselves. The most noticeable feature remains

the marked difference in glyceride structure between the majority of seed fats and the other classes of natural fats which have been mentioned.

Table III.

Fats.	Acids in whole fat.				Fully-saturated glyceride content.	
	Weight.		Molecules.			
	Saturated.	Un- saturated.	Saturated.	Un- saturated.	Weight.	Molecules.

Vegetable Seed-fats.

	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Coconut (CN)	91.7	8.3	93.9	6.1	84	86
Dika (D)	89.4	10.6	91.7	8.3	79	80.5
Nutmeg butter (N)	88.6	11.8	90.2	9.8	71	73.5
Palm kernel (PK)	80.8	19.2	85.3	14.7	63	66.5
Borneo (Illipé) tallow						
(I)	62.0	38.0	62.6	37.4	4.5	4.5
Cacao butter (CB)	58.8	41.2	60.0	40.0	2.5	2.5
Kusum oil (K)	35.5	64.5	37.5	62.5	1.2	ca. 1
Cottonseed oil (CS)	23.4	76.6	25.0	75.0	1(?)	below 1
Ground-nut oil (GN)	15.1	84.9	15.3	84.7	1(?)	below 1

Vegetable Pericarp Fats and Animal Fats.

Stillingia tallow (S1)	65.5	34.5	66.8	33.2	23.5	24
" " (S2)	70.4	29.6	72.5	27.5	27.5	28.5
Palm oils (P1)	48.6	51.4	50.9	49.1	10	10.5
" (P2)	46.9	53.1	49.2	50.8	9	9.5
" (P3)	41.6	58.4	43.7	56.3	7	7.5
" (P4)	47.0	53.0	49.1	50.9	8	8.5
Butter fats (B1)	61.3	38.7	67.3	32.7	31	34
" (B2)	59.9	40.1	66.1	33.9	29	31.5
Buffalo ghee (BG)	64.2	35.8	70.1	29.9	32	34
Cow ghee (CG)	62.0	38.0	67.5	32.5	32	33
Mutton tallow (MT)	59.7	40.3	61.5	38.5	26	26.5
Beef tallow (BT)	47.9	52.1	50.0	50.0	13.5	14
Lard (L)	44.1	55.9	46.0	54.0	9	9.5
Rabbit fat (R)	31.9	68.1	34.0	66.0	7	7.5

(CN), (PK)—Collin and Hilditch, 'J. Soc. Chem. Ind.,' vol. 47, p. 261T (1928).

(D), (N)—Collin and Hilditch, 'Biochem. J.,' vol. 23, p. 1273 (1929).

(I)—Hilditch and Priestman, 'J. Soc. Chem. Ind.,' vol. 49, p. 197T (1930).

(CB)—Lea, 'J. Soc. Chem. Ind.,' vol. 48, p. 41T (1929).

(K)—Dhingra, Hilditch and Vickery, 'J. Soc. Chem. Ind.,' vol. 48, p. 281T (1929).

(CS)—Hilditch and Lea, 'J. Chem. Soc.,' p. 3106 (1927).

(GN), (BT)—Christian and Hilditch, 'Analyst,' vol. 55, p. 75 (1930).

(S1), (S2)—Hilditch and Priestman (forthcoming publication).

(P1) to (P4)—Hilditch and Jones (Miss), 'J. Soc. Chem. Ind.,' vol. 49, p. 363T (1930).

(B1), (B2)—Hilditch and Jones (Miss), 'Analyst,' vol. 54, p. 75 (1929).

(BG), (CG)—Bhattacharya and Hilditch (forthcoming publication).

(MT)—Collin, Hilditch and Lea, 'J. Soc. Chem. Ind.,' vol. 48, p. 46T (1929).

(L)—Hilditch and Sleightholme (unpublished observation).

(R)—Vickery (private communication).

We do not propose to discuss at any length the implication of these figures, since there is at present little basis for logical deductions. The approximation of animal fats and vegetable pericarp fats in glyceride structure to those obtained by direct laboratory synthesis leaves open the possibility that such fats are actually built up in the living organism from glycerol and fatty acids and it is, of course, accepted that such processes take place in the liver during the course of fat metabolism. The characteristic structure of seed fats, on the other hand, is difficult to reconcile with any ordinary process of ester synthesis. There may possibly be some connection here between the observed glyceride structure and the fact that in the vegetable both glycerol and fatty acid are being elaborated from a different class of compound (*e.g.*, carbohydrates), although it is difficult to see why the same argument, if valid, should not apply to pericarp fats. It is perhaps more easy at the moment to conceive the phenomenon of "evenly distributed" glyceride structure in seed-fats as the result of direct formation of glycerides from non-fatty compounds than as the consequence of combination of separately produced molecules of glycerol and fatty acids.

Summary.

Synthetic triglycerides have been prepared from various combinations of lauric, palmitic or stearic acids with unsaturated acids (85 per cent. oleic and 15 per cent. linoleic acid). The fully-saturated glyceride contents of the synthetic fats, when plotted in molar percentages against the molar percentage of saturated acids present in the mixture of fatty acids esterified, lie on a smooth curve.

The corresponding values for a number of animal fats, including tallows and butter fats, and for some vegetable pericarp fats, appear to lie close to, but not coincident with, the curve for the synthetic glycerides; the animal fats contain as a rule somewhat more, whilst the pericarp fats appear to contain somewhat less, fully-saturated glycerides than the synthetic fats for a given ratio of saturated to unsaturated acids.

On the other hand, vegetable seed fats are almost invariably assembled on entirely different principles, the glyceride structure being determined by a tendency to "even distribution" of the fatty acids amongst the glycerol molecules; in seed fats, fully-saturated glycerides rarely appear in appreciable quantity until the molar proportion of saturated acids in the mixed fatty acids reaches about 60 per cent.

Acknowledgment is made to the Government of the Central Provinces of India for a Research Scholarship held by one of us (R. B.) during the course of this work.

Experiments with High Velocity Positive Ions.

By J. D. COCKCROFT, Fellow of St. John's College, Cambridge, and E. T. S. WALTON, 1851 Overseas Student.

(Communicated by Sir Ernest Rutherford, P.R.S.—Received August 19, 1930.)

[PLATE 21A.]

1. *Introduction.*

It would appear to be very important to develop an additional line of attack on problems of the atomic nucleus. The greater part of our information on the structure of the nucleus has come from experiments with α -particles and if we can supplement these with sources of positive ions accelerated by high potentials we should have an experimental weapon which would have many advantages over the α -particle. It would, in the first place, be much greater in intensity than α -particle sources, since one microampere of positive ions is equivalent, so far as numbers of particles is concerned, to 180 grams of radium equivalent. It would in addition have the advantage of being free from penetrating β and γ rays which are a complication in many experiments, whilst the velocity would be variable at will.

The main difficulty in obtaining such sources lies of course in the production and application of the very high potentials necessary to accelerate the particles if velocities approaching that of the α -particle are to be obtained. For example, α -particles from polonium have an energy corresponding to 5.2 million electron volts and a potential of 2.6 million volts would be required to give a helium nucleus an equal amount of energy. We have therefore to decide what is the minimum acceleration voltage at which we can usefully work, since the experimental difficulties increase very rapidly with increasing voltage. In making this decision we are naturally guided by the recent theoretical work of Gamow* on the "Theory of Artificial Disintegration." On Gamow's theory the probability of an α -particle of velocity v entering a nucleus of atomic number Z , after coming within the effective radius of the nucleus, is

$$W = e^{-\frac{16\pi e^2 Z}{\hbar v} J_k},$$

where J_k is a function varying slowly with v and Z . It is clear, therefore, that for particles of equal energy the lighter particle has the greater chance of

* 'Z. Physik.,' vol. 52, p. 514 (1929).

penetration into the nucleus, so that we should choose protons as our source of positive ions for this reason.

Values of W for a proton of 300 KV. entering different elements are given in Table I. We tabulate also their closest distance of approach for a head-on collision on the classical theory.

Table I.

Element.	H.	Be.	B.	C.	Al.	α -particle from Polonium in Al.
W	—	$6 \cdot 2 \cdot 10^{-3}$	$1 \cdot 2 \cdot 10^{-3}$	$2 \cdot 1 \cdot 10^{-4}$	$(9) 10^{-5}$	0.65
b	$4 \cdot 8 \cdot 10^{-13}$	$1 \cdot 9 \cdot 10^{-12}$	$2 \cdot 4 \cdot 10^{-12}$	$2 \cdot 88 \cdot 10^{-12}$	$6 \cdot 2 \cdot 10^{-12}$	—

The voltage of 300 KV. was chosen because it appeared quite possible to begin work on a laboratory scale with voltages of this order and to develop vacuum tubes which would withstand such potentials. It appears from this table that there is at any rate some chance of obtaining results of interest in experiments on artificial disintegration and on scattering of protons by different elements. From unpublished results of Blackett the range of a 300 KV. proton in air should be about 5 mm., so that it might be possible to study their effects in the Wilson expansion chamber.

In addition to experiments of this type, great interest attaches to experiments on the radiation produced by protons on impact with matter. So far experiments have been carried out with protons up to 55 KV.* velocity and no evidence has been obtained of any continuous or characteristic radiation. The experiments of Bothe and Franz† on the Excitation of Characteristic Radiations by Polonium α -particles show, however, that the intensity of the radiation varies approximately as the ninth power of the velocity of the particle so that it is well worth while investigating the problem with 300 KV. protons. The very much greater intensity attained with proton sources might be expected to offset the decrease in intensity due to the lower velocity. There is also the very interesting point as to whether a nuclear radiation of the type discovered by Bothe and Becker,‡ resulting from the bombardment of light elements with polonium α -particles, can be excited by proton impacts.

* Barton, 'J. Franklin Inst.,' vol. 209, p. 1 (1930); Gerthsen, 'Ann. Phys.,' vol. 85, p. 881 (1928).

† 'Z. Physik,' vol. 52, p. 466 (1928).

‡ 'Naturwiss,' August 8, 1930.

2. Methods of Production of High Velocity Positive Ions.

The problem may be divided into two parts: first, the production of a stream of positive ions in a form suitable for acceleration, and second, the method of acceleration. It is unfortunate that sources of protons cannot be obtained as simply as sources of positive ions of the alkali metals. It was found possible, for example, to develop a very simple tube in which sources of sodium ions obtained from a Kunsman mixture could be accelerated by potentials up to 200 KV. and there is no doubt that this tube would have withstood the potentials of 300 KV. which were later available. In the search for an equally simple source of protons, experiments were made similar to those of Barton (*loc. cit.*) on the production of protons by the diffusion of hydrogen through a tube into a strong electric field. A platinum tube of diameter 0.25 mm. was surrounded concentrically by a cylindrical cathode. The platinum tube was heated to 1350° C. and hydrogen allowed to diffuse through. A potential of 20 KV. was then applied between tube and anode giving a field of 400 KV. per centimetre at the surface of the tube, a field of the order of fifty times that used by Barton. It was thought possible that increased ionisation of the issuing gas might result, but no positive result was obtained.

We had thus to fall back on the low voltage arc or the canal ray tube as a source of hydrogen ions. The low voltage arc has the advantage that the ions produced are more homogeneous in velocity than the ions from a canal ray tube, but it was found that the pencil of ions so produced was very much less intense at the end of the metre path necessary for the accelerating chamber, than in the case of the canal ray tube ions. With the canal ray tube, sources of ions of several micro-amperes could be obtained after acceleration and this method was therefore chosen.

In considering methods of acceleration of the ions, four sources of potential suggest themselves for consideration—Tesla coils, impulse voltages, low frequency alternating potentials and rectified steady potentials. If it is desired simply to obtain the highest possible potentials with the minimum of trouble then the Tesla coil is obviously the ideal solution. Breit and Tuve* claim for example, to have produced voltages of several millions with a Tesla coil wound on a metre length of Pyrex tubing and experiments by Dr. Allibon† in the Cavendish Laboratory have shown that the Tesla coil can be used successfully for certain types of experiments with electrons. It has, however, the serious disadvantage that the average time during which the maximum

* 'Phys. Rev.', vol. 35, p. 51 (1930).

† In course of publication.

voltage occurs is usually only about one-thousandth of the total time, so that the intensity of the stream produced is very low when dealing with a limited source of ions as in positive ion work. Its main application would appear to be in experiments of the Wilson chamber type in which only very weak sources of ions are required.

The impulse generator allows a unidirectional voltage impulse to be obtained by connecting in series a number of condensers charged in parallel. The maximum value of the impulse may reach several million volts, its duration being several micro seconds. This method suffers still more seriously from the disadvantages of the Tesla coil in its short time of application, but has the advantage over the Tesla coil in that most dielectrics will withstand a much greater stress for a few micro seconds than when subjected to an oscillatory voltage of the Tesla type.

By the third method, low frequency alternating potential, voltages of over a million may be obtained by connecting transformers in cascade, the only limitation to the voltages obtainable being expense and space. If alternating voltages are used for the acceleration of the ions, both positive and negative ions will be obtained from a canal ray tube source and ions of all velocities will be present. This would necessitate, first, a rectified source of excitation for the canal ray tube since high voltage electrons cause very serious interference with all experiments, due to the X-rays produced. Secondly, it would be necessary to apply magnetic analysis to obtain a homogeneous beam of ions and the source obtained would be weakened. It is clear therefore that the ideal accelerating voltage is a steady potential produced by rectifying the current from a low frequency transformer. Since the current required is only a few micro amperes the potential may be smoothed very completely by a condenser of a few thousandths of a micro farad capacity and the stream of ions produced may be expected to have a very uniform velocity. It was therefore decided to construct a thermionic rectifier for 300 KV. which would at a later stage allow of extension to 600 KV. if this was required by the experiments. For this purpose the well-known circuit of fig. 1 is used in which two kenetrons A are connected in series to withstand the doubled voltage in the non-conducting half cycle. The canal ray tube is excited by a separate 60 KV. transformer F, the whole of which is raised to a potential of 300 KV. above earth, the primary being supplied by a special insulation transformer G.

If it is desired at a later stage to double the voltage it would be necessary to add a second Kenetron unit, and condenser, with an insulating transformer to supply the primary of the high tension transformer.

Having decided on a unit to generate 300 KV. the difficulty at once arose that no commercial rectifiers existed which would withstand voltages of more

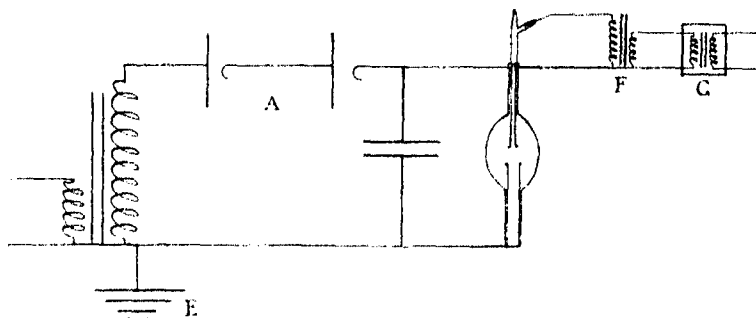


FIG. 1.

than 220 KV., so that three or four Kenetrons would be required for the purpose, with double the number for the higher voltage. This complication is very undesirable if only on grounds of expense, for puncture of one Kenetron may lead to the failure of the rest. As, however, the experiments of Dr. Allibone on high voltage Lenard tubes had resulted in the development of a continuously evacuated tube which would withstand 350 KV., it seemed certain that a continuously evacuated Kenetron could be produced which would enable the necessary 300 KV. to be obtained with one unit. After a few experiments with different sizes of tubes and different electrode arrangements, we were finally successful in developing a suitable type of rectifier.

For the supply of the high voltage, a transformer giving 350 KV. with one end earthed was designed by the Research Staff of the Metropolitan-Vickers Electrical Company, particular attention being paid to compactness in design. The current output of the transformer is 60 milliamps, an output necessitated not by the small experimental current required but by the capacity current of the apparatus at high potential, a capacity of 100 cm. requiring a charging current of 15 milliamperes at 250 KV. The transformer primary is excited by a motor generator set giving smooth control of the voltage by variation of the generator field, special control switch gear being installed to eliminate switching surges. The secondary voltage is determined by rectifying and measuring the charging current of a small condenser formed by a band on the outside of the transformer bushing and the high tension lead.

A unipivot galvanometer G combined with a frequency meter allows the voltage to be determined with an accuracy of 1 per cent., a calibration being carried out in the first place with a standard sphere gap.

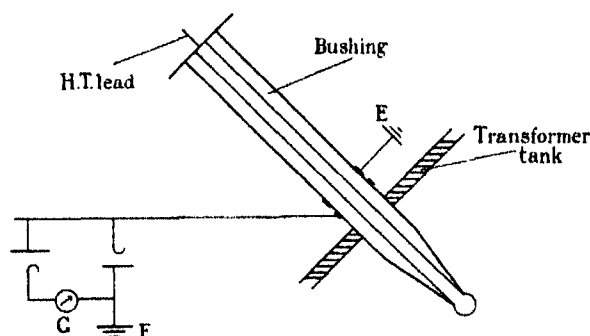


FIG. 2.

3. Rectifying Apparatus.

A considerable amount of experimental work was carried out before a suitable design for the thermionic rectifiers was evolved. The sparking distance for 300 KV. between points in air is 100 cm. and the tubes used must be longer than this to allow room for suitable corona shields at each end. If the size of the bulb on the tube is too small the glass gets charged up in isolated patches by auto electronic emission from the electrodes, even though the electrodes have been designed to avoid sharp corners and have been well polished. As the voltage is raised, surface creepage sparks ("Gleitfunken") result and can be seen running from one side of the bulb to the opposite side, puncture usually following very soon. To prevent this, the bulb should be large and the glass should be thick and of a high dielectric strength. On the recommendation of Dr. Gunther Schultze, the bulbs finally used were blown from a hard "molybdenum" glass by the Jena Glaswerke. The bulb diameter was 30 cm. and the stems were 5 and 9 cm. in diameter respectively.

Various types of filament and electrode design were tried. In order to prevent electrons from reaching the walls of the bulb, the anodes were made from nickel plated copper vessels which at first almost completely surrounded the cathode. To prevent the large electrostatic forces from distorting the filament, the latter was placed just inside the end of a steel shield. This produced a poor type of characteristic as shown by curve A in fig. 3, the voltage drop being excessive due to space charge. The filament was then exposed by pushing up the shield and, after a number of trials, it was found that a V-shaped filament, supported at the ends and in the middle, was not deformed by the voltages used. The filament was made of 0.25 mm. tungsten wire and was placed about 5 cm. in front of the anode, the characteristic for this arrangement

being given by curve B, fig. 3. All the metal parts were outgassed *in vacuo* before assembly and the anodes were outgassed *in situ* by electron bombardment

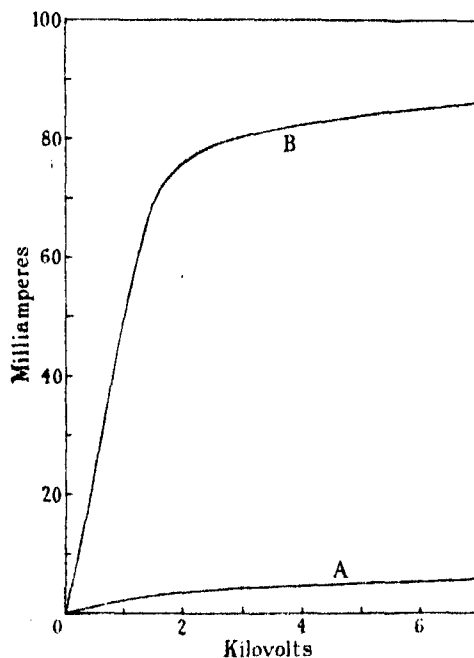


FIG. 3.

from the filament. With this type of rectifier it was found possible to produce 150 KV. direct current and thus two in series should give 300 KV. direct current.

Since the rectifiers are to be continuously evacuated and since each end of them has to be at high potential, it is necessary to pump out through a tube which will stand the full potential. The most convenient arrangement appeared to be to join the two rectifiers end to end and to pump out through a third bulb similar to that used for the rectifiers. The whole forms a large T-piece and is shown to scale in fig. 4. As shown in this diagram, the insulation bulb has tubular electrodes fitted, which distribute the electrical stress properly and so prevent puncture of the glass. The pump used is a three-stage oil diffusion pump designed by Burch.* The speed of the pump is 20 litres per second and full advantage of this can be taken as no liquid air trap was

* 'Proc. Roy. Soc.,' A, vol. 123, p. 271 (1929). (We are indebted to Metropolitan-Vickers Electrical Company for supplying us with several of these pumps before they had been put on the market.)

necessary. This type of pump has been found to be very satisfactory. Its speed was evident during the outgassing of the anodes. The bombarding

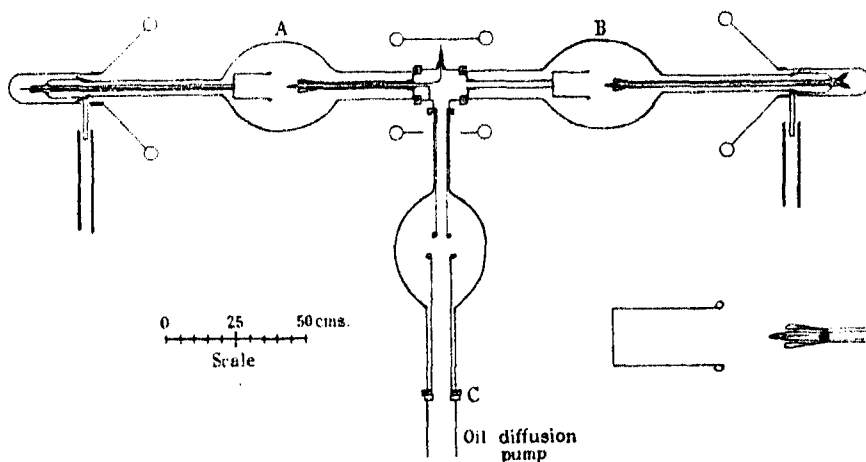


FIG. 4.

potential used caused the tubes to go "soft" when the gas was liberated. On switching off this potential for only a few seconds, the large volume of gas in the three bulbs was found to have been completely exhausted. The only disadvantage which oil has as compared with mercury is that it is necessary to be careful that air is not admitted to the apparatus while the oil is hot.

The three bulbs are joined together by waxing them into a steel T-piece. The insulation bulb carries most of the weight and is supported directly on top of the pump. It is connected to the latter by a flat steel to steel ground joint to which it is waxed. The outer ends of the bulbs are supported on long Bakelite tubes. This general design of rectifier results in an economy of space, of a pump and of a bulb. It has the further advantage that if one rectifier accidentally goes "soft" the other goes "soft" too, and it thus avoids puncture of the glass by the extra potential thrown upon it. Corona shields, as shown in fig. 4, are fitted at each end of the tubes and in the middle to prevent puncture of the glass stems. At first these were placed at the extreme ends of the rectifiers and a number of punctures were obtained through the glass at the junction of the stem to the bulb. It was found that this could be avoided by moving the shields considerably nearer to the bulbs of each rectifier. When a puncture through the glass occurs, it was found that the leak produced can be very readily stopped by painting over the hole with cellulose enamel.

The filaments were originally heated from oil-immersed transformers, but

as it proved impossible to get these to stand a potential greater than 250 KV. without using excessive dimensions it seemed simplest to substitute accumulators. These are placed inside round boxes to prevent brushing and are insulated from earth by Bakelite cylinders.

In order to secure an equal distribution of potential between the rectifiers, it is necessary that the various capacities present should be properly balanced. It can be seen that the capacity between the electrodes in the insulating bulb and the capacity of the accumulators for heating the filament in bulb A are effectively in parallel with the capacity of bulb B. The capacities involved are small and the following appeared to be the simplest way of obtaining the correct size of balancing condenser. A sphere gap C, D was connected to the extreme ends of the rectifiers A and B as shown in fig. 5. A third sphere

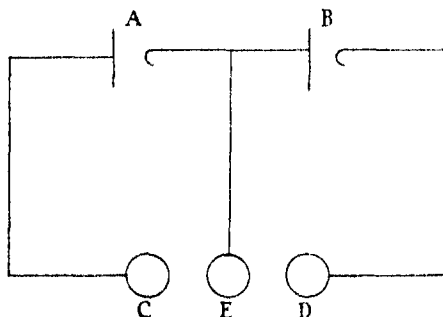


FIG. 5.

E was suspended symmetrically between the spheres C and D by fine wire and was connected to the junction of the rectifiers A and B. A small voltage was then applied to the rectifiers and if the potential across A exceeded that across B, then the force between C and E was greater than that between D and E, with the result that E would move towards C. In this way it was possible to adjust the capacity of the balancing condenser much more accurately than was required. The spheres could then be removed without disturbing the balance as they had introduced equal capacities across the two rectifiers. The balancing capacity required was about 40 cm., and was made from about a dozen glass dielectric, parallel plate condensers connected in series. These were stacked one on top of the other and separated by distance pieces so that spark over in air would not occur between the first and last condensers.

The current from the rectifiers is smoothed by a 0.002 μ F condenser.

4. Design of Tube for Producing Fast Protons.

The direct potential obtained by the method just described, is applied to a large bulb similar to that used for the rectifiers. As shown in fig. 6, the bulb is

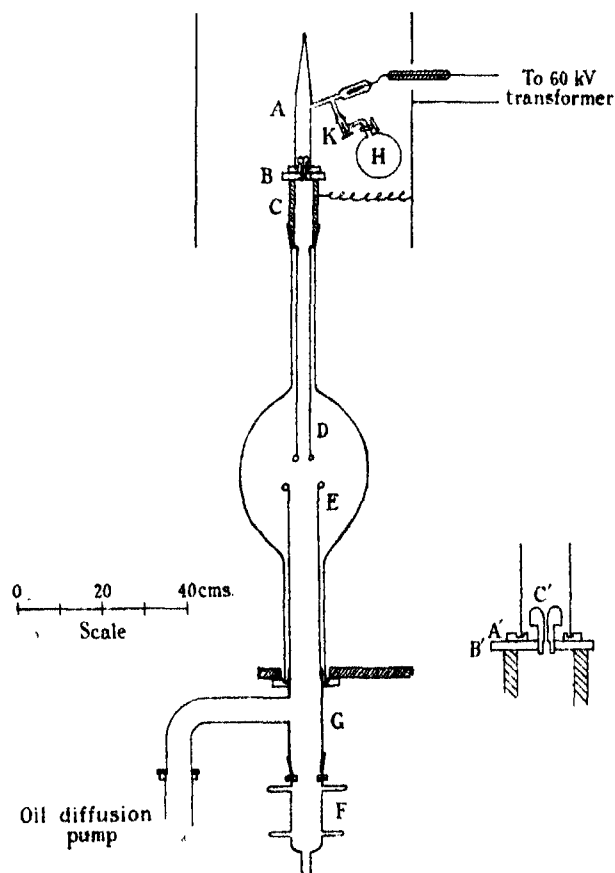


FIG. 6.

fitted with tubular electrodes, D, E of the type used in the insulation bulb, the upper electrode D being screwed to the steel section of a steel to glass ground joint connecting the bulb with the canal ray tube. The canal ray tube, A, is of the Wien type and is waxed into a groove in a flat steel ground joint A'. This can be moved over another ground flat surface B', which is soldered to the top of the tube C. A good vacuum-tight joint can easily be made by running a little low vapour pressure grease* round the outside. By the adoption of

* Burch, *loc. cit.*

this device, the canal ray tube can be moved with respect to the anode C', whilst the tube is under vacuum and very accurate adjustment is possible. The importance of this adjustment is shown by our obtaining an increase by a factor of five in the positive ion current reaching the experimental chamber F.

The experimental chamber consists of a length of 3-inch diameter glass tubing with suitable side stems, waxed into one section of a conical steel to steel ground joint. The other section of the joint is soldered to a wax cup holding the accelerating tube. The joint is made tight by running "picein" over it with a small flame. A short piece of 2-inch diameter steam pipe connects the tube G to a fast Burch oil diffusion pump of the same pattern as used on the rectifiers. Very fast pumping is thereby attained.

The positive ions are produced by a discharge in hydrogen excited by an alternating voltage of between 40 and 60 KV. The positive ions pass through a canal 1.5 mm. in diameter and 10 mm. long, the electrode shape being made identical with that used by Dr. Aston in his mass spectrograph. After passing through the canal the stream of ions pass down the axis of the tubular electrode D and are accelerated to a speed corresponding to the potential applied to the tube when they reach the space between the electrodes D and E. A continuous flow of hydrogen from a storage bulb is admitted to the tube through a variable leak of the Kaye type.

In preliminary experiments a diaphragm was placed in the tube C to define the beam more closely. With this arrangement it proved to be necessary to use an additional diffusion pump to evacuate the space between the anode and the diaphragm, as without this additional pumping a great deal of neutralisation of the ions occurred. Fortunately it was found possible to remove this diaphragm altogether and dispense entirely with the extra pump, the Burch pump being quite capable of dealing with the leak with a potential of 300 KV. on the accelerating bulb. The addition of a pumping system at a potential of 300 KV. above earth would have been a serious complication in the apparatus.

The transformer for exciting the canal ray tube is raised to a potential of 300 KV. by the rectifiers and has to be supported on an insulating pedestal and shielded from corona by a cylindrical sheet of galvanised iron. As shown in fig. 1 its primary winding is excited by a one to one insulation transformer of the type described by Blackett and Hudson.* A spacing of 5 inches is used between primary and secondary and the whole is immersed in a Bakelite tube filled with very carefully purified transformer oil.

* 'J. Sci. Instruments,' vol. 5, p. 391 (1928).

As the canal ray tube is at a high potential above earth and has a number of sharp-edged metallic parts it is fitted with a corona shield of galvanised iron. A photograph of the whole apparatus is shown on Plate 21A.

5. Operation of the Apparatus.

On starting up the apparatus after several hours' rest we find that the rectifiers usually go soft at a comparatively low voltage, perhaps 80 KV. Immediately the discharge occurs the transformer voltage drops to a very small value for a few seconds until the pumps have dealt with the gas evolved. The voltage will then rise again and may be increased to perhaps double the value until a further evolution of gas occurs. After 1 or 2 minutes operation, stable working can be obtained. The hydrogen is then admitted and the position of the canal ray tube adjusted to give a maximum current in the experimental chamber. Once adjusted, of course no further movement is required in subsequent experiments. The pressure in the tube is next adjusted by the Kaye leak to give a maximum current in the experimental chamber. This usually occurs when the pressure is such as to cause green fluorescence over most of the glass, the potential applied then being 40 to 50 KV. and the current through the tube about one-third of a milliampere. It is usually possible to obtain a total current to a collecting electrode in the chamber F of the order of 10 microamperes. Unfortunately the greater part of this is due to secondary electron emission, and the application of a retarding potential to prevent escape of the secondaries reduces the total current by a factor of five.

Experiments were first carried out with a Willemite screen in the experimental chamber to determine the spread of the stream of ions. It was found that, as the accelerating voltage was increased, focussing of the stream occurred at about 80 KV. accelerating potential. The stream then produces a star-shaped pattern on the screen which disappears as the voltage is increased still higher. It seems probable that this focussing is produced by the radial component of the accelerating field inside the high tension accelerating electrode D, since the corresponding radial field in the low tension electrode E will have a negligible effect owing to the high velocity of the ions at this point. If this explanation is correct, it would appear possible to obtain focussing at any desired velocity by choice of the geometry of the accelerating electrodes. At the highest voltages, the stream was concentrated in a circle about 4 cm. diameter, the distribution of intensity being very clearly shown by the discoloration of a metal diaphragm placed in the path.

A magnetic analysis of the stream was carried out in order to determine the relative numbers of protons and molecules. A narrow beam was defined by a diaphragm and the protons and molecules were collected on separate targets after deflection. It was found that with the pressures used in the discharge tube, the number of protons was approximately equal to the number of molecules.

6. Experimental Work in Progress.

Experimental work of a preliminary character has been carried out with the mixed stream of protons and molecules at voltages up to 280 KV. in order to decide whether any radiation is produced by their impact on matter.

Using targets of lead and a beryllium salt successively, very definite indications of a radiation of a non-homogeneous type were found, using a gold leaf electroscope as a detector. By absorption measurements, the average hardness of the radiation from lead at 280 KV. would appear to be about 40 KV., but harder components were present which will require further investigation before any definite statement can be made. Control experiments were carried out to eliminate the possibility of the radiation being produced by spurious sources such as the canal ray tube or secondary electrons. The intensity of the radiation was of the order of one ten-thousandth of that produced by an equal electron source and increased extremely rapidly between 250 and 280 KV. No marked difference in intensity was observed between the radiation from beryllium and lead.

We are very much indebted to Mr. A. P. M. Fleming, Mr. G. McKerrow, Mr. B. L. Goodlet and other members of the research staff of the Metropolitan-Vickers Electrical Company for very considerable technical assistance and for the loan of apparatus.

One of us (E. T. S. W.) is indebted to the Royal Commissioners for the Exhibition of 1851 for the grant of an Overseas Research Scholarship.

We have finally to express our thanks to Sir Ernest Rutherford for his encouragement and advice throughout this work.

The Scattering of Light in Protein Solutions. I.—Gelatin Solutions and Gels.

By K. KRISHNAMURTI, D.Sc., University College, London.

(Communicated by F. G. Donnan, F.R.S.—Received May 26, 1930.)

[PLATE 21B.]

In a previous paper,* the investigation of the scattering of light in agar sols and gels was described and a view regarding the changes taking place in the system during gelation was developed.

In a series of papers, of which this is the first, the author proposes to publish investigations of the scattering of light in protein solutions. The various physical properties of the different proteins have been studied for a long time past. Several workers have tried to evaluate the molecular weights of the proteins from the osmotic pressure of their solutions and also from analytical data. Recently a very precise and definite method for the determination of the molecular weights of the proteins, based upon the sedimentation of these heavy molecules in the ultra-centrifuge, has been successfully developed by Svedberg.† The molecular weight can be determined in two ways:—(I) by the measurement of the sedimentation equilibrium reached in the cell as a result of the centrifugal and diffusion forces; (II) by measuring the sedimentation velocity of the protein molecules in high centrifugal fields.

It has been found by Svedberg‡ and his co-workers that all native proteins so far studied can be divided into two large groups; the hæmocyanins with molecular weights of the order of millions and all other proteins with molecular weights, ranging from about 85,000 to about 210,000. They divide the second of the above groups into four sub-groups. The molecular mass, size and shape are about the same for all proteins belonging to the same sub-group. They have also made the interesting discovery that the molecular masses characteristic of the three higher sub-groups can be derived from the molecular mass of the first sub-group by multiplying by the integers *two*, *three* and *six*. Further, several of these proteins have been shown to be uniform with regard to the mass and size of the particles. It is therefore of interest to investigate

* 'Proc. Roy. Soc.,' A, vol. 122, p. 76 (1929).

† Svedberg and co-workers. 'J. Amer. Chem. Soc.,' vols. 48, 49, 50 51.

‡ 'Nature,' vol. 123, p. 871 (1929).

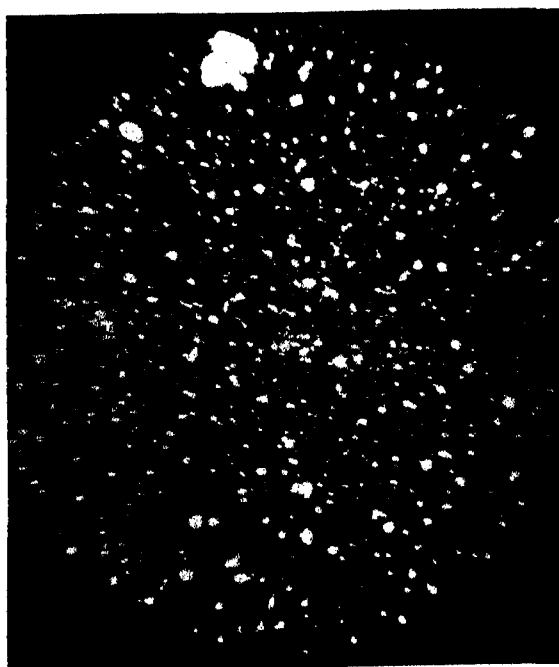
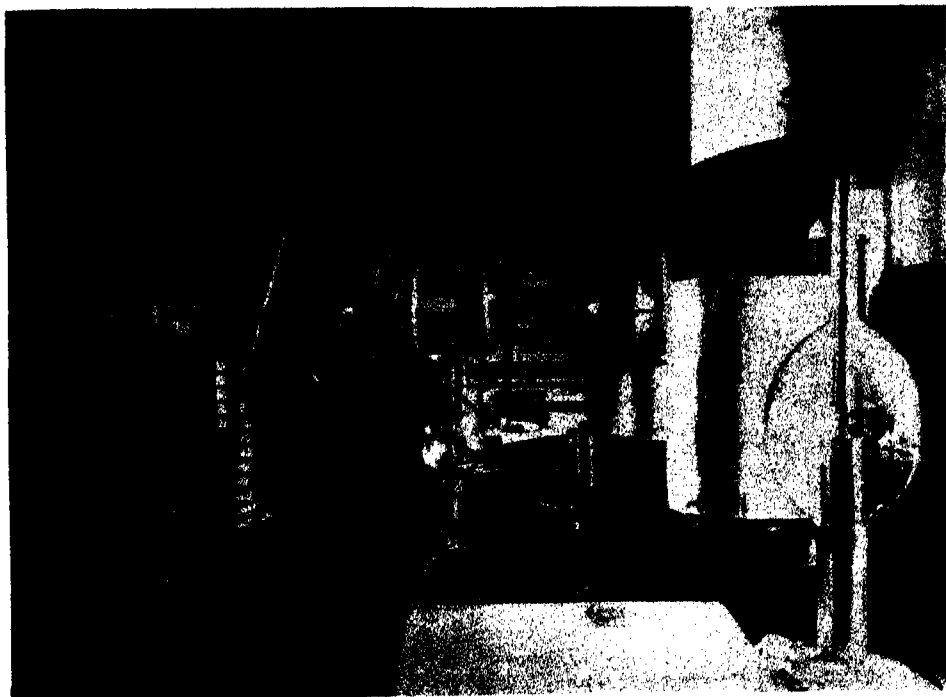


FIG. 3.

(Facing p. 400.)

the scattering of light in solutions of these proteins, in order to get further information regarding the relative changes in the size and shape of the protein molecules and their aggregates under different conditions of temperature, concentration, ageing, etc. Some of the proteins that are being investigated are gelatin, egg-albumin, and casein. The present paper deals with the scattering of light in gelatin solutions and gels.

Arisz* was the first to study the Tyndall effect in glycerol-sols of gelatin. He used a photographic method for determining the order of the intensity of the scattered light and found that the intensity of the Tyndall cone depends upon the temperature, the previous history of the gelatin, and the concentration, the intensity being greater the lower the temperature and the greater the concentration of the sol. He attributes the increase in Tyndall effect to the coalescence of the gelatin particles.

More recently Kraemer and Dexter† have made a quantitative study of the effect of the hydrogen-ion concentration on the Tyndall effect in gelatin sols. They found a sharp rise in Tyndall intensity at the isoelectric point at and below 25 degrees, but at about 40 degrees the variation in p_H had no marked effect on the light scattering capacity of gelatin sols. They made use of this observation to locate the isoelectric point in gelatins from various sources and their mixtures.

In spite of the very extensive investigations on gelatin there does not appear to be any clear agreement between the views of different workers regarding the condition of gelatin in the sol state. For a better understanding of the nature of these systems and of the process of gel-formation, it was thought desirable to investigate in detail the effect of temperature, time, concentration, etc., on the intensity and depolarisation of the scattered light. It has been shown in the previous paper on agar sols how such a study led to interesting conclusions regarding the nature of agar sols and gels.

Experimental.

The apparatus used in this investigation for the measurement of the intensity of the scattered light is described below and shown in fig. 1.

P is the tungsten arc of a pointolite lamp (1000 candle power), L is a lens for obtaining a nearly parallel beam of light. S_1 and S_2 are circular slits of suitable diameter, placed in the path of the incident beam so as to cut off the stray light. One portion of this beam of light passes through another slit S_3 ,

* 'Kolloidchemische Beihefte,' vol. 7, p. 22 (1915).

† 'J. Phys. Chem.,' vol. 31, p. 764 (1927).

non-reflecting black. The scattered beams enter the observation box through two suitable apertures.

The apparatus for measuring the depolarisation of the scattered light has been already described in a previous paper.*

Preparation of gelatin solutions.—The gelatin used was first purified by Loeb's method, viz., washing several times with an acetic acid solution of p_H about 4.8, and then repeatedly with distilled water, after which it was dried. The ash content was found to be 0.12 per cent. A weighed quantity of the purified gelatin in the form of powder was stirred with the required amount of water in an Erlenmeyer flask, and allowed to swell for several hours. Then it was heated to about 60 degrees when it quickly passes into solution. The solutions thus obtained were filtered through filter paper to remove any suspended particles and were thus rendered quite clear and transparent.

RESULTS AND DISCUSSION.

Effect of Temperature on the Scattering of Light in Gelatin Solutions and Gels.

When a gelatin solution of say 2 per cent. concentration is cooled below 20 degrees it sets to a gel. The reverse process, viz., gel-sol transformation can be brought about by heating the gel, although the temperature required to effect this conversion is much higher than the "setting point." Thus, the gelatin solutions, like those of agar, exhibit marked "hysteresis," though not to the same extent as the latter. The formation of the gelatin gels is further characterised by a marked increase in the light scattering capacity in a short region about the isoelectric point of gelatin, viz., p_H 4.8. This has been studied by Arisz, Kraemer and others (*loc. cit.*). But the point of interest is that, when the p_H is about 3, gel formation takes place without any change in the Tyndall intensity whatever. The following investigation deals with the changes in the intensity and depolarisation of the scattered light during gelation. The results obtained are significant in relation to questions such as the nature of gelatin sols and their gel-formation. Table I gives the results obtained with a 2 per cent. gelatin solution at the isoelectric point. The figures in column 2 express the "Tyndall number," or the ratio of the intensity of the light scattered by gelatin sols to that of the standard. In column 3 are given the corresponding values of the depolarisation factor, i.e., the ratio of the intensity of the weak component to that of the strong component in the scattered light.

* 'Proc. Roy. Soc.,' A, vol. 122, p. 83 (1929).

Table I.—Sol-gel transformation. Two per cent. gelatin sol, $p_H=4.8$.

Temperature.	Intensity of Scattered Light.	Depolarisation Factor.
°		
50	7.8	0.038
45	7.8	0.038
40	7.8	0.038
35	7.8	0.038
30	7.8	0.038
25	8.5	0.038
23	9.0	0.034
22	12.0	0.034
21	16.3	0.038
20	27.1	0.045
19	37.6	0.053
18	48.8	0.072
	(set to gel)	
17	—	0.119
16	85.0	0.155
15	—	0.198
10	140.0	0.455
(after several hours)		

The following points can be noticed from the above results :—

- (1) There is no appreciable change in the intensity of the scattered light as the sol is cooled from 50° to 25°, but at 25° a steady rise commences, and as the temperature is still further lowered the Tyndall number increases rapidly. The sol sets to a gel at 18°. The variation of Tyndall number with temperature is shown clearly in fig. 2. It must be mentioned here that the Tyndall intensity is not only a function of temperature, but also of time.
- (2) There is a marked increase in the Tyndall number before the sol sets to a gel. No abrupt change is noticed at the setting point.
- (3) Besides the intensity, the depolarisation factor (θ) of the scattered light also undergoes marked changes during the sol-gel transformation. As the sol is cooled below 25° a small decrease in the value of θ is first noticed till 22°, but below this temperature the depolarisation increases again.

Discussion.—It will be seen that the above results are very similar to those obtained in the case of agar sols in all essential points. In a previous paper, the nature of agar sols and their gel-formation has been discussed and a view put forward. It is here proposed to extend the same view to gelatin solutions; for a careful examination shows that all the facts observed in the case of gelatin sols can be satisfactorily explained from that point of view.

Gelatin sols above 30° can be considered to be polydisperse systems, in which at least part of the gelatin is present in the molecularly dispersed

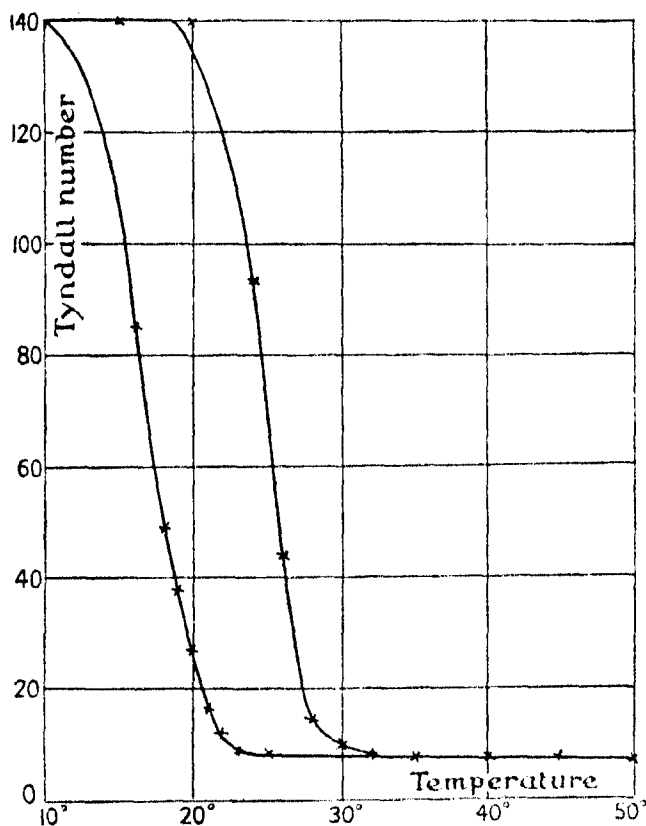


FIG. 2.

condition, and the rest as polymolecular micells. The extent to which a particular sol is molecularly dispersed depends upon its concentration. It appears very probable that in weak gelatin sols of about 0.5 per cent. concentration, the gelatin is molecularly dispersed to a large extent, whereas in concentrated sols (say 4 per cent.) the colloidal content is very much greater. When a dilute gelatin solution at p_{H} 4.8 is cooled below 25° , the intermicellary liquid probably becomes supersaturated, and this leads to the formation of molecular aggregates. The particles thus formed become larger due to the further condensation of molecular gelatin.

A glance at fig. 2 shows that below 25° there is a sudden and steep rise in

the Tyndall intensity. This seems to indicate that there is a tendency for gelatin to precipitate from a solution which has become supersaturated.

It has been pointed out above that as the temperature is lowered below 25° the intensity of the scattered light increases steadily, whereas the depolarisation factor first decreases and then increases. The explanation offered for a similar phenomenon observed in the case of agar sols was that, as the molecular aggregates are increasing in size their spherical symmetry also increases at the same time. This suggestion is a perfectly natural one and is therefore extended to the present case of gelatin sols. It has to be mentioned here that the very high values of the Tyndall number and depolarisation attained at 10° after several hours may be due to subsequent aggregation of these colloidal particles formed previously. It is possible that the values of the Tyndall intensity in the case of the very turbid sols are not accurate, but considerably lower than what they would be if the incident beam was not diminished in intensity after passing through a portion of the turbid sol or gel.

Ultramicroscopic Examination during the Sol-gel Transformation.

In order to test how far the above view is correct, an ultramicroscopic examination of gelatin sols of various concentrations at p_H 4.8 during the process of gel-formation was undertaken. When viewed in a cardioid ultramicroscope with strong illumination, gelatin sols above 30° appear to be completely homogeneous. Only a particle here and there is visible. As the cooling proceeds a large number of very fine particles in Brownian motion appear after a time. It is possible to find, at this stage, that the particles are of very different sizes. Some of them are so small as to be just visible in the ultramicroscope, while others are much larger. It may be interesting to mention here that the very fine particles appear to be bluish in colour, *i.e.*, the light scattered by them is richer in the shorter wave-lengths. The very large ones scatter white light. This is, in fact, what one observes in macroscopic light scattering. Gradually, the smaller particles begin to form aggregates. In the earlier stages of aggregation it is still possible to detect Brownian motion of the aggregates. Occasionally, the particles form chains, and when these are not long, they show a tendency to twist and turn about. Gradually, the Brownian motion of the coarser particles and their aggregates ceases, while that of the smaller ones still continues. On leaving the gel at 12° for several hours, the whole field of view becomes filled with innumerable particles, which are just visible and are very close to one another (*cf.* fig. 3, Plate 21B).

Another interesting point which may be mentioned is that the separate particles, as seen in the ultramicroscope, are spherical in shape.

It will be seen therefore that the ultramicroscopic examination lends strong support to the views developed before regarding the mechanism of the sol-gel transformation.

Gel-sol transformation.—When a 2 per cent. isoelectric gelatin gel is heated, it gradually becomes less turbid, and at about 28° it is converted into a sol. The following table gives the changes in intensity and depolarisation of scattered light at different temperatures during the gel-sol transformation.

Table II.—Gel-sol transformation. Two per cent. gelatin gel,
 $p_H = 4.8$.

Temperature.	Intensity of Scattered Light.	Depolarisation Factor.
10	140.0	0.455
15	140.0	0.455
20	140.0	0.455
24	93.0	0.260
26	43.5	0.106
28	14.6	0.038
(melted to sol)		
30	9.8	0.038
32	8.5	0.038
35	7.8	0.038

It will be seen from the above results that the intensity of the scattered light does not change appreciably till about 20°, but above this temperature the Tyndall number as well as the depolarisation factor gradually decrease, until the system is converted into a sol. During this "melting" of the gel there is no abrupt change in the light scattering. This clearly indicates that though the gel remains quite rigid, the gel micells gradually become smaller. If aggregation of the colloidal particles in the original sol were responsible for the gel formation, we should expect an abrupt decrease in the light scattering capacity during the melting of the gel. Such is not actually the case. The gel micells gradually pass back into the state of the original molecular dispersion during the warming.

Ultramicroscopic Examination during the Gel-sol Transformation.

It is of interest to examine how far the above view is in accord with facts. An ultramicroscopic examination of the changes taking place during the gel-sol transformation was therefore made.

A gelatin gel (2 per cent.) at p_H 4.8, when examined in a cardioid ultra-microscope, is found to consist of a multitude of extremely fine particles very close to one another, and also some larger particles and their aggregates (*cf.* fig. 3). When this gel is slowly warmed, it is found that the particles and their aggregates become smaller and gradually disappear. Finally, the whole field of view appears quite uniform and homogeneous just as it was when the original sol was examined.

It can be seen from the above how a parallel study of the changes in the intensity and depolarisation of the scattered light during the formation of gels and of the ultramicroscopic fields gives very valuable information regarding changes in the size and shape of the particles.

The question naturally arises whether the changes described above are connected with the formation of gels, or if they take place altogether independently of gelation. To answer this question, it is necessary to examine the changes of the light scattering in gelatin sols of very low concentration as the temperature is lowered. A 0.5 per cent. solution (p_H — 4.8) is very suitable for the purpose ; for, on cooling even to 10° , it remains in the sol state, though it becomes very turbid. The results in Table III show the variation of the intensity and depolarisation (θ) of the scattered light with temperature.

Table III.—0.5 per cent. gelatin sol— p_H 4.8.

Temperature.	Intensity of Scattered Light.	Depolarisation Factor (θ).
40	2.3	0.038
30	2.3	0.038
28	2.4	0.038
25	2.6	0.038
23	2.8	0.034
22	—	0.031
21	3.1	0.028
20	3.3	0.025
18	3.7	0.020
15	5.6	0.025
12	8.7	—
8 (after several hours)	34.8	0.053

The following facts will be clear from the above results :—

- (1) The intensity of the scattered light is small at 40° , and as the temperature is lowered a steady increase in Tyndall number takes place at and below 25° .

- (2) The increase in Tyndall number till 12° is not so marked as in the case of the more concentrated sols ; but it reaches a high value when the sol is kept at 8° for several hours.
- (3) Below 25° the depolarisation factor decreases until a small value is reached at 18° , below which it slowly increases again. The value of θ obtained at 8° after the sol has been kept for some hours is quite high.

It will thus be seen that the behaviour of the 0.5 per cent. gelatin sol is exactly similar to that of the more concentrated sols. From the above it can be seen that, when a dilute sol ($p_H = 4.8$) is cooled, it still remains in the sol state, though it becomes very opalescent. On the other hand, a 2 per cent. sol of $p_H 3$ sets to a rigid gel on cooling without any increase in the light scattering. These facts clearly indicate that the increase in turbidity observed when gelatin sols are cooled (at the isoelectric point), is not connected with their gel-formation.

When the turbid 0.5 per cent. gelatin sol (at 8°) is warmed, it gradually becomes clear again. A careful examination of the changes in the intensity and depolarisation of the scattered light during the process has revealed certain interesting points. The results are given in Table IV.

Table IV.—0.5 per cent. gelatin sol— $p_H = 4.8$.

Temperature.	Intensity of Scattered Light.	Depolarisation Factor (θ).
10°	34.8	0.053
15	34.8	0.053
20	27.5	0.038
22	23.2	0.038
25	10.6	0.020
28	3.0	0.025
30	2.8	0.025
34	2.3	0.034

The above results show that—

- (1) As the temperature is raised there is no appreciable change in Tyndall number or the depolarisation factor till 20° , above which they both rapidly decrease.
- (2) At 25° a minimum value of θ is reached, and above this temperature the depolarisation factor again increases, though the Tyndall intensity diminishes.

The explanation suggested for the effects observed above is that, as the temperature is raised above 20° , the micells in the opalescent sol gradually decrease in size, and probably also become more unsymmetrical in shape. A decrease in size causes a corresponding decrease in the value of depolarisation (θ), whereas a departure from spherical symmetry increases the value of θ . Above 25° the second factor has the greater influence, and hence the value of θ increases, although the Tyndall number decreases. This effect is exactly the reverse of that observed during the cooling of the sol.

A significant point is that above 30° there is only a very slight decrease in Tyndall number, whereas θ increases quite appreciably. This apparently corresponds to the change taking place in the micells during the final stage of their splitting up into the gelatin molecules contained in the original sol. It evidently shows that—

- (1) The particles or molecules of gelatin in the clear sol above 35° are more unsymmetrical in shape than the polymolecular micells present in the opalescent sol at 30° .
- (2) These particles must be small in size.

Another possible way of explaining all the results obtained above was suggested by a rather surprising observation made by the author, namely, that a very turbid gelatin gel at the isoelectric point, when dried in a desiccator, becomes quite clear by the time the gel shrinks to about two-thirds of its original volume. It appears likely from this observation that the removal of turbidity in gelatin gels is connected with the shrinking of the micells. It appeared at first sight that lowering of the temperature of gelatin sols at the isoelectric point below 25° causes a swelling of the individual micells, which therefore increase in volume and also tend to become more spherical in shape, thus accounting for the very marked increase in the intensity of the scattered light, as well as the changes in the depolarisation factor. Such a view seems at first sight quite probable in view of the fact that, since the heat of swelling is positive, according to the principles of thermodynamics, we should expect an increase of swelling with lowering of temperature. But this view involves several difficulties, viz. :—

(1) Pieces of gelatin become opalescent when allowed to swell in water. But this is very small compared to the marked turbidity shown by (say 2 per cent.) gelatin gels at the isoelectric point. This indicates that swelling of the micells is not the main factor responsible for the turbidity of the gelatin gels.

(2) Swelling of gelatin is a maximum at p_H about 3, so that it is natural to

expect, according to the above view, a marked turbidity in gelatin gels at this p_H . But actually gel-formation takes place at this p_H without an increase in the Tyndall intensity of the sol.

(3) It has been mentioned above that the turbid gelatin gel becomes clear during the process of dehydration in a desiccator. If this partially dried, clear gel be again kept in contact with water the original turbidity is not restored.

(4) The sedimentation velocity of the particles in the ultracentrifuge is a measure of their relative masses. It has been found by the author, during an ultracentrifugal study of gelatin solutions* (0.4 per cent.) of different p_H values, that near the isoelectric point the sedimentation constant obtained, even with freshly prepared solutions is quite high and shows a considerable increase with age. In fact, at p_H 4.8, the particles in a gelatin solution (kept for a day after preparation) sediment almost completely in a very short time. On the other hand, at and below p_H 4.0 and also at p_H 7.5 the sedimentation constant is much lower than that at p_H 4.8, and ageing has practically no effect on it. This certainly indicates that at p_H 4.8 a very marked aggregation of the gelatin molecules takes place. A mere increase in the hydration of the particles on cooling gelatin sols, causing an increase in their size, cannot explain the enormous increase in the sedimentation constant of the particles at p_H 4.8.

The turbidity of gelatin gels at the isoelectric point is probably caused by the formation of loose molecular aggregates of gelatin, enmeshing a part of the water in a loose state of combination. This view is supported by an interesting observation made by the author, viz., the clearing up of a turbid 2 per cent. gelatin gel during (a) its dehydration in a desiccator,† and (b) the diffusion of dilute hydrochloric acid into the gel. The loose water within the aggregates of gelatin molecules is thus extracted (in the first case by dehydration, and in the second probably by the osmotic pressure exerted by the acid solution in the intermicellary space), and this causes a shrinkage of the micells, and hence a diminution of the light scattering capacity. It appears unlikely that either the dehydration of the gel or the diffusion of the dilute acid into it will cause a decrease in the refractive index of the micells (relative to that of the intermicellary water) to an extent sufficient to explain the loss of turbidity of the gel.

* Carried out in the laboratory of Prof. Svedberg at Upsala.

† K. Krishnamurti, 'Nature,' vol. 123, p. 243 (1929).

The Molecular State of Gelatin Solutions.

There does not appear to be any clear agreement between the views of different workers regarding the condition of gelatin in the sol state. Some workers regard gelatin solutions as molecularly dispersed, while others maintain that they are distinctly colloidal. In fact, Thomas Graham* himself gives gelatin as a typical example of a colloid, his chief consideration being based on the low diffusibility of the particles. Recently, however, Svedberg and his co-workers (*loc. cit.*) have shown that, in spite of the very high molecular weights and the low diffusion constants of proteins, they possess certain properties which are characteristic of molecular dispersions, viz., uniformity of the particles with regard to mass and size. This is a point of difference between molecular dispersions and typical colloidal sols. Thus, in all colloidal solutions a great variation in the size of the particles is observed. Even in the case of gold sols prepared according to Zsigmondy's nuclear method, which were previously supposed to be uniform with regard to particle size, it has been shown quite definitely by Rinde† by means of the ultracentrifuge, that these sols are polydisperse. Again, the particles of the proteins to which Svedberg assigns definite molecular weights, have been shown to behave in the centrifugal field as the *smallest units* in these solutions. The change in the molecular weight caused by the aggregation of these particles, which takes place under certain conditions of temperature and p_H value, has been shown to be reversible. On the other hand, in solutions of high acidity and alkalinity these protein particles are decomposed into smaller units, and this change is an irreversible process. Thus, the protein particles have been shown to be uniform with regard to mass and size, and also that no other particles smaller than these are present in an undecomposed protein solution.

It is admitted by many investigators that the proteins combine with acids and bases in stoichiometrical proportions,‡ and that this combination can be interpreted better by considering the chemical nature of the protein particles than their surface properties. Thus, the ultimate particles in protein solutions appear to function as definite chemical entities.

From the above considerations it seems justifiable to regard the protein particles as molecules. It may therefore be permissible to use the word "molecules" for the units in gelatin solutions, since gelatin is known to be a typical protein.

* 'Phil. Trans.,' vol. 151, p. 183 (1861).

† Dissertation, Upsala (1928).

‡ T. B. Robertson—J. Alexander's "Colloid Chemistry," vol. 2, p. 255 (1928).

In a previous section of this paper the view was put forward that gelatin sols may be considered to be polydisperse systems, in which at least part of the gelatin is present in the molecularly dispersed condition, and the rest as polymolecular micells; and the extent to which a particular sol is molecularly dispersed depends upon its concentration and temperature. This view has been found to be useful in explaining the results obtained by the author, specially in connection with the variation of the intensity of the scattered light with the concentration of gelatin sols and gels. It is of interest to examine how far this is supported by the ultracentrifugal study of gelatin sols. It was possible to work conveniently only with sols of 0.4 per cent. concentration in the centrifuge. It was found that in the region of p_H 4.6—6.0, a marked aggregation of the gelatin molecules takes place, and at the same time the gelatin sols become very heterogeneous. Even at and below p_H 4.0 and at p_H 7.5, where there is no aggregation of gelatin molecules, the sols have been found to be heterogeneous, and the values of the molecular weight determined at various distances from the centre of rotation (in the ultracentrifuge), vary from about 70,000 to 10,000. From the above it is clear that the heterogeneity observed in gelatin solutions is due partly to the aggregation of gelatin molecules, and partly to the presence of some of the products of decomposition of gelatin.

Variation of the Intensity of Scattered Light with the Concentration of Gelatin Sols and Gels.

The light scattering capacity of gelatin sols depends not only upon the temperature, but also on the concentration. An examination of the intensity of the scattered light in the sols and gel states at different concentrations will give us an idea of the extent to which the sols are colloidal dispersions. The results are given in Table V.

Table V.—Gelatin Sols and Gels— $p_H = 4.8$.

Concentration.	Intensity of Scattered Light.		$\frac{\text{Tyndall int. in gel.}}{\text{Tyndall int. in sol.}}$
	Sol state (40°).	Gel. state (12°).*	
per cent.			
0.5	1.5	23.1	15.4
1.0	3.0	50.0	16.7
2.0	7.5	66.7	8.8
4.0	7.5	43.0	5.7
6.0	7.5	17.7	2.4
8.0	7.5	10.9	1.4

* Kept at 12° for some hours.

It will be seen that the intensity of the scattered light in the sol state increases with concentration till about 2 per cent., after which further increase in concentration does not appreciably alter the Tyndall intensity. The relation between the concentration and Tyndall number is rather complicated at high concentrations, where due to the close packing of the particles there might be mutual interference.

But, what is more interesting is that, when these gelatin sols are cooled to 12°, and kept at this temperature for some hours, the more dilute gels are comparatively more turbid. In fact, the Tyndall number reaches a maximum with the 2 per cent. gel, above which the intensity gradually falls off. It is difficult to interpret these results on the assumption that the gelatin sols are purely colloidal dispersions and that lowering of the temperature brings about their aggregation, which increases the light scattering capacity of the system. For, according to this view, the increase in the Tyndall intensity should be more pronounced in the case of the more concentrated sols. On the other hand, the view put forward by the author, viz., that gelatin sols may be considered to be polydisperse systems, in which the proportion of molecularly dispersed gelatin increases with the dilution of the sol, gives us a simple and satisfactory explanation of the above results. Lowering the temperature below 20° has the effect of producing supersaturation, as a result of which loose molecular aggregates of gelatin are formed. If this view were correct we should expect the ratio of the Tyndall number in the gel state to that in the corresponding sol, which is a measure of the amount of molecular gelatin that has aggregated, would be greater in the dilute sols than the more concentrated ones. The results in Table V (last column) are actually in accord with this explanation.

Variation of the Depolarisation of Scattered Light with Temperature and Concentration.

It has already been mentioned in a previous section that the depolarisation factor of the light scattered by a gelatin sol decreases at first and then increases very markedly as the temperature is lowered below 25°. It is of interest to examine how this behaviour is effected by the change in concentration of the sol. The results obtained with gelatin sols of 2 per cent., 1 per cent. and 0.5 per cent. concentrations at various temperatures are given in Table VI.

It can be seen from the results that in the case of the 2 per cent. sol, the decrease of θ between 25° and 22° is small, whereas with sols of 1 and 0.5 per cent. concentrations, the initial decrease in the value of θ is very pronounced. In general, the lower the concentration of the sol, the more marked is this

effect. A similar phenomenon has been observed in the case of agar sols. It will be further noted that the initial decrease in θ takes place at about the same temperature, viz., 23° , i.e., when the Tyndall number has commenced to increase. The significance of this will be clear from the explanation suggested in a previous section and briefly given below.

Table VI.—Gelatin sols ; $p_H = 4.8$.

Temperature.	Depolarisation factor (θ).		
	2 per cent. sol	1 per cent. sol	0.5 per cent. sol
°			
40	0.038	0.038	0.038
35	0.038	0.038	0.038
30	0.038	0.038	0.038
25	0.038	0.038	0.038
24	0.038	0.034	—
23	0.034	0.031	0.034
22	0.034	0.031	0.031
21	0.038	0.031	0.028
20	0.045	0.028	0.025
19	0.053	0.028	—
18	0.072	0.031	0.020
17	0.119	—	—
16	0.155	0.045	—
15	0.198	0.082	0.025
14	—	—	0.025
10 (after several hours)	0.455	0.180	0.053

When the gelatin sols are cooled below 25° they become supersaturated, and this brings about the formation of fresh micells. This is followed by the condensation of the molecularly dispersed gelatin, thus increasing the size of the particles. The intensity of the scattered light increases in all cases. But the change in the depolarisation factor is determined by the size as well as the shape of the particles. An increase in the size of the particles causes a corresponding increase in the value of θ , whereas an increase in the spherical symmetry of the particles will lower the value of θ . It seems very probable that, during the growth of the particles, they tend to become more spherical due to the symmetrical condensation of gelatin on them. Thus, the value of θ is influenced by two factors, which act in opposite directions, and whichever is more appreciable will have the greater effect.

In the case of dilute gelatin sols (0.5 per cent.), we are probably concerned with molecular aggregation to a large extent, and hence the tendency for the formation of more spherical particles is very pronounced ; and hence θ decreases.

On the other hand, in the 2 per cent. sols the rapid aggregation of gelatin molecules probably leads to the formation of coarser particles and hence the increase in θ is more conspicuous.

It may be interesting to mention in this connection the recent work of S. R. Rao,* who observed similar effects, viz., the decrease and the subsequent increase in the optical anisotropy as the molecular association in liquids like acetic, propionic and butyric acids, and some aromatic liquids, *e.g.*, nitrobenzene, increases. The similarity between these results and those obtained during the cooling of agar and gelatin sols strongly indicates the similarity in the nature of the two processes. It therefore appears very probable that the effects observed when gelatin sols are cooled below 25° are really due to the aggregation of gelatin molecules.

A comparison of the values of θ in gelatin sols of the different concentrations in the sol and gel states (*c.f.* Table VII) shows that θ at 40° does not vary with concentration, whereas at 10° the difference is very marked. It appears that at 10° the colloidal micells present in the more concentrated gels are bigger than those contained in the weaker ones.

Table VII.

Concentration.	θ in sol state, 40°.	θ at 10°
per cent.		
2.0	0.038	0.455
1.0	0.038	0.180
0.5	0.038	0.053

Effect of Acids and Bases on the Scattering of Light in Gelatin Sols and Gels.

The effect of hydrogen-ion concentration on the Tyndall effect in gelatin sols has been studied by several workers and more carefully by Kraemer and Dexter (*loc. cit.*). They have observed that the Tyndall intensity rises sharply at the isoelectric point of gelatin (viz., p_H 4.8—4.9) below 25°, but at about 40° the variation in p_H has no appreciable effect on the light scattering capacity of gelatin sols. Recently the author has made an ultracentrifugal study of gelatin sols at different p_H values in Prof. Svedberg's laboratory at Upsala. It was found that :—

* 'Indian J. Physics,' vol. 1, p. 1 (1928).

- (1) Within a region of p_H between 4.6 and 6.0, the sedimentation constant (S) is quite high; and further there is a considerable increase of S with age, the more so the nearer the solution is to the isoelectric point. In fact, at p_H 4.8 the particles in the sol, that has been kept for a day at room temperature, sediment almost completely in a very short time.
- (2) At and below p_H 4.0 and p_H 7.5 the sedimentation constant is much lower, and ageing has practically no effect on it.

Judging from the parallelism between the Tyndall intensity and the sedimentation constant in gelatin sols at different p_H values, it is clear that the marked turbidity near the isoelectric point is caused by the aggregation of gelatin particles. It is difficult to say with certainty whether this tendency for precipitation is to be interpreted in terms of the simple ampholyte solubility or as the flocculation of colloidal micells of gelatin. The author is, however, inclined to the view that the effectiveness of acid or base in preventing the precipitation of gelatin is due to the capacity of the acid or alkali to combine with gelatin, thereby increasing its solubility, so that lowering of the temperature does not cause a supersaturation of the solution and the precipitation of gelatin.

It is well known* that when a little alcohol is added to a gelatin solution near the isoelectric point, a rapid precipitation of gelatin occurs. If, however, the p_H is 4.4 or below, or above 5.0, the tendency for precipitation is reduced to nil even when an excess of alcohol is added. It will be interesting to compare this with the p_H -Tyndall number curve obtained by Kraemer. He found an extremely pronounced maximum at the isoelectric point, but, when enough acid was added to bring the sol to p_H 4.6, the gelatin was transformed into a condition in which the light scattering capacity of the sol is practically unchanged on lowering the temperature. Thus, the parallelism between this effect and the extent of precipitation with alcohol appears to be a striking fact in favour of the above view.

Summary.

(1) The effect of temperature on the intensity and depolarisation of the light scattered by gelatin sols and gels has been investigated; and a view regarding the nature of gelation has been put forward. Gelatin sols have been considered to be polydisperse systems, in which part of the gelatin is present in the molecularly dispersed condition, and the rest as polymolecular micells.

* cf. Loeb's "Proteins and Theory of Colloidal Behaviour," p. 251 (1922).

Cooling the sol below 25° produces supersaturation, as a result of which fresh particles are formed, and these become larger due to the condensation of the molecularly dispersed gelatin on them.

(2) An ultracentrifugal examination of gelatin sols at p_H 4.8 shows clearly that a considerable aggregation of gelatin molecules takes place at this p_H . This is also supported by an ultramicroscopic examination.

(3) During the gel-sol transformation the gel-micells are gradually dispersed into the original molecular condition.

(4) The molecular state of gelatin in the sols is discussed, and reasons are put forward to justify the use of the term " molecules " for the protein particles.

(5) The variation of the intensity of the scattered light with the concentration of gelatin sols and gels has been examined. At about 40° the Tyndall number increases with concentration up to 4 per cent. gelatin content, above which it remains constant. But, when these sols are cooled to about 10° the dilute sols are much more turbid than the concentrated ones. An explanation of this observation has been offered.

(6) A careful examination of the variation in the depolarisation (θ) of the scattered light when gelatin sols of different concentrations are cooled to 10° , reveals certain interesting facts. θ decreases at first and then increases; and this effect is more pronounced in the case of dilute sols. The significance of this phenomenon in revealing the changes in the size and shape of the micells has been pointed out.

(7) Judging from the parallelism between the Tyndall intensity and the sedimentation constant in gelatin sols at different p_H values it is clear that the turbidity near the isoelectric point is caused by the aggregation of gelatin molecules. The author is inclined to the view that the effectiveness of acid or base in preventing the precipitation of gelatin is due to the capacity of acid or alkali to combine with gelatin, thereby increasing its solubility, so that lowering of the temperature does not cause a supersaturation of the solution and the precipitation of gelatin.

The author desires to express his best thanks to Prof. F. G. Donnan, C.B.E., F.R.S., for his very kind interest in this work.

The Nature and Size of the Luminescent Centre.

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PART I.—*Solid Solutions.*

There is considerable evidence that the luminescence of most inorganic solids is due to the solid solution of a trace of an activator in another substance (*e.g.*, Bi in CaS), and that absolutely pure salts do not show luminescence.* Lenard has suggested that the absorbing and re-emitting centre in such cases consists of an atom or molecule of the activator linked with a definite number of the solvent molecules and attributes each luminescent band to a different centre.† As to the nature of the association, there is evidence that it consists of the replacement of one of the metallic ions or atoms of the solvent lattice by one of the activating atoms. It has been shown for instance by Tiede and Schleede that luminescent solid solutions have a definite crystal structure whose lattice dimensions differ slightly from those of the pure solvent.‡ Gruhl has produced samples of zinc silicate phosphors each showing a different luminescent band and each having a correspondingly different crystal structure.§

It is the object of this paper to show that simple assumptions in line with these ideas lead to a relation between brightness of luminescence and concentration of the activator which is in accord with experimental results and which gives an explanation of the existence of an optimum concentration. Further it will be shown that the experimental determination of this relation leads to a value of the number of molecules in a centre.

Several attempts have been made by previous workers to investigate and explain the relation between brightness of luminescence and concentration of activator. Bruninghaus|| arrived at the law

$$F = A \cdot c \cdot e^{-Kc}, \quad (1)$$

from experiments on cathodoluminescence, where c is the molecular concentration of the activator and A , K are constants. Merritt has criticised Bruning-

* "Handbuch der Physik," vols. 21, 23.

† 'Sitz. Heidelb. Akad.,' 1917, 1918; "Handbuch der Physik," vol. 23.

‡ 'Tiede and Schleede,' Z. Electrochem. 29 (1923).

§ Gruhl, Dissert, Berlin, 1923; "Handbuch der Physik," vol. 23.

|| 'C. B.,' vol. 149, p. 1375 (1909).

haus treatment and results* showing that the assumptions made in explaining it are not in accord with subsequent work, and has developed a new theory leading to the relation

$$I = A \cdot \frac{c}{a + c} \cdot e^{-Kc}, \quad (2)$$

for which experimental confirmation is claimed from results obtained with solid solutions of uranium salts. Now since the uranium salts were themselves luminescent when pure, in some cases being nearly as bright as the optimum brightness of the solid solutions, the experimental evidence is hardly convincing. Moreover some of the assumptions made by Merritt in developing the theory are not justified. Thus, in making allowance for the effect of absorption on the brightness, Merritt assumes (a) that the solvent has appreciable absorption coefficients for the exciting light and for the emitted light, and (b) that the absorption due to the activating material increases proportionally with the concentration. As regards assumption (a), experimental evidence goes to show that the solvents used in luminescent solid solutions are transparent over a region extending from the infra-red to far into the ultra-violet.† This fact would make the constant a in the relation deduced by Merritt equal to zero and the expression would reduce to the form

$$I = A \cdot e^{-Kc},$$

which gives no explanation of the existence of an optimum concentration.

As regards assumption (b), measurements by the writer on luminescent liquid solutions show that in these cases, the absorption does not increase proportionally to the concentration (see Part 2 of this paper), so that it is doubtful whether this assumption is safe in the case of solid solutions. It may be shown, however, that it is possible to derive an expression similar to that of Bruninghaus by reasoning in accord with recent knowledge of luminescent solid solutions and free from the doubtful assumptions used by Merritt.

Let us suppose with Lenard, that a luminescent centre, responsible for a given band in emission, consists of a definite number of solvent molecules associated with one molecule of the activator B. The process of making a luminescent solid solution involves some way of bringing about an intimate mixture of A and B either in the solid state or from a mixed solution in a common solvent; so that the resulting distribution in the solid solution is a random one. Consider any random choice of a small volume v of the solid

* 'J. Opt. Soc. Amer.,' vol. 12, p. 613 (1924).

† Pohl and Rupp, 'Ann. Physik,' vol. 81, p. 1161 (1926), *inter alia*.

solution containing $n + 1$ molecules of both kinds together. The chance that this will contain one molecule of B and n of A is obviously

$${}^NC_1 \cdot {}^MC_n / {}^{M+N}C_{n+1}$$

(where N = total number of B molecules present, M = total number of A molecules present) which may be written (since M and $N \gg n \gg 1$)

$$\doteq N \cdot \frac{M^n}{n!} \bigg/ \frac{(M+N)^{n+1}}{(n+1)!} = N \cdot M^n (n+1) / (M+N)^{n+1}. \quad \text{The number of}$$

centres then (one molecule of B to n of A) is given by the product of the total possible number of trials of different small volumes v and the chance of a centre occurring in a given trial, *i.e.*, the number of centres = $N \cdot M^n \cdot (n+1) / (M+N)^{n+1} \cdot M + N / n + 1 = N \cdot M^n / (M+N)^n = N / (1 + N/M)^n = M \cdot c \cdot (1+c)^{-n} \doteq M \cdot c \cdot e^{-nc}$ (since c is very small), where c = molecular concentration of B in A.

The brightness of the luminescence will depend on the number of centres, the intensity of the exciting light and the absorption of the exciting and emitted light in the solution. Consider a thin layer of the luminescent solid solution of thickness t and unit cross section, illuminated by exciting light of intensity I .

The layer dy at a depth y below the surface will contain $M \cdot c \cdot e^{-nc} \cdot dy$ centres (where M is the number of A molecules per c.c.).

The number of centres in this layer activated by the exciting light will be proportional to the intensity of the exciting light at this depth. Experiments on luminescent liquid solutions (see Part 2 of this paper) show that while the absorption coefficients for the exciting and emitted light are dependent on the concentration, there appears to be no simple relation between the two. We shall, therefore, put f_1 and f_2 for the absorption coefficients for the exciting and emitted light respectively, f_1 and f_2 being unknown functions of the concentration. Then the light emitted from the layer dy is given by

$$K \cdot I \cdot M \cdot c \cdot e^{-nc} \cdot dy \cdot e^{-f_1 \cdot y},$$

where K is a constant including the probability of an encounter between an exciting quant and a centre. Making allowance now for the absorption of this emitted light in passing through the thickness y of the solution the contribution of the layer dy to the total luminescence on the side towards the incident light is

$$dF = K \cdot I \cdot M \cdot c \cdot e^{-nc} \cdot e^{-(f_1+f_2)y} \cdot dy$$

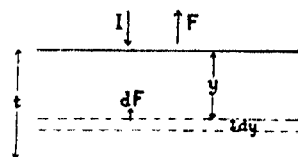


FIG. 1.

and integrating for the whole thickness t the total luminescence is given by

$$F = \int_0^t P \cdot c \cdot e^{-nc} \cdot e^{-(f_1+f_2)y} \cdot dy = P \cdot c \cdot e^{-nc} [1 - e^{-(f_1+f_2)t}] / (f_1 + f_2).$$

(Putting $K \cdot I = P$.)

Now, as we have already mentioned, experimental evidence shows that the pure solvents used in luminescent solid solutions are transparent far into the ultra-violet, and since, for the small concentrations of activator necessary for measurable luminescence, the solid solutions show no colour, we may assume that $(f_1 + f_2)$ is not large. If in addition we work with very thin layers of the solid solution, it is justifiable to assume that $(f_1 + f_2)t$ is small enough to write

$$1 - e^{-(f_1+f_2)t} = (f_1 + f_2)t,$$

whence we arrive at an expression similar to that of Bruninghaus

$$F = P \cdot c \cdot e^{-nc} \cdot t = A \cdot c \cdot e^{-nc}. \quad (3)$$

$$\text{Putting } A = P \cdot t.$$

Or, if there are a number of different centres each with its own characteristic value for n we shall have

$$F = A \cdot c \cdot e^{-n_1c} + B \cdot c \cdot e^{-n_2c} + \dots \quad (4)$$

Differentiating the expression (3) (one band) with respect to c , we get

$$dF/dc = A [-c \cdot n \cdot e^{-nc} + e^{-nc}] = Ae^{-nc} [1 - nc],$$

and since F is a maximum when $dF/dc = 0$, the optimum concentration is given by $c = 1/n$, so that a determination of the optimum concentration gives the value of n .

Experimental Arrangements.

In carrying out a quantitative test of the above relation it is necessary to prepare luminescent solid solutions whose concentrations may be varied and determined and whose brightness is large enough to be measured with reasonable accuracy.

The substances chosen as being suitable were solid solutions formed by the intimate mixture and subsequent heating of Sb_2O_3 , Bi_2O_3 and PbO , respectively, in CaO .

The antimony oxide was mixed dry while the lead and bismuth oxides were first converted into the nitrates in aqueous solution and then mixed into a paste with the CaO and dried. All samples were heated to the same tempera-

ture (600° C.) under the same conditions of time and rate, in quartz tubes in an electric furnace. Separate tests were made to ensure that under these conditions none of the activator was evaporated off. The exciting light was from a mercury vapour lamp through a Uviol screen 3 mm. in thickness, which excluded the visible region. In order to ensure constancy of illumination the lamp was served through a rheostat which was adjusted so that at the moment of observation the voltage across the lamp was at a predetermined value. With this precaution, it was found that the intensity of illumination from the lamp remained very constant.

The brightness of the samples, which were placed in a tray close to the lamp window, was measured with a Holophane lumeter in conjunction with a colour screen, which passed the luminescent radiations, in the eyepiece.

With this instrument it was found possible to repeat observations on the same sample at different times with variations of readings of about 3 per cent., so that the measurements given below, which represent the means of a number of readings should not be in error by more than about 1 per cent.

Experimental Results.

Considering the relation deduced above for the luminescence due to one centre (one band)

$$F = A \cdot c \cdot e^{-nc},$$

we have taking logs to base 10

$$\log F/c = \log A - (n \log e) C,$$

so that in the case of luminescent solid solutions showing only one band, a linear relation should exist between $\log F/c$ and c , the slope of the line giving the value of $n \log e$ and hence n and the intercept on the $\log F/c$ axis giving the value of the constant A . Fortunately, in the cases of the antimony and lead solutions only one band was shown in each case. As seen in the direct vision spectroscope these were

Antimony :—*Circa* 6000–5000 Å. Colour of luminescence, greenish yellow.

Lead :—Very broad band with maximum at about 6000 Å. Colour of luminescence, deep yellow.

The results of plotting $\log F/c$ against c with these two sets of solid solutions, taking c as the atomic concentration of Sb/Ca and Pb/Ca respectively, are shown in figs. 2 and 3.

It will be observed that the linear relation to be expected from the theory is very fairly followed.

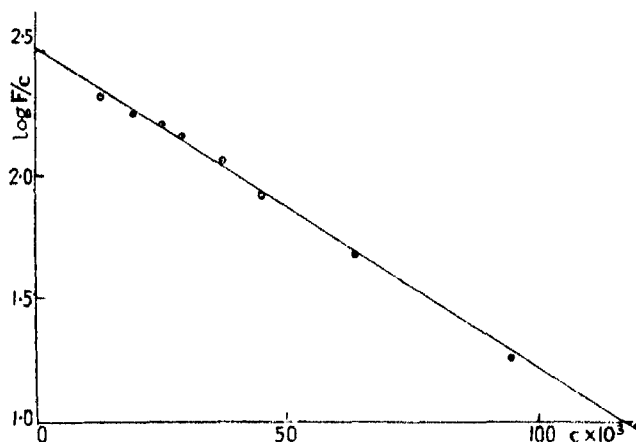


FIG. 2.—CaOSb. $F = Ace^{-nc}$. $n = 30$. $A = 324$.

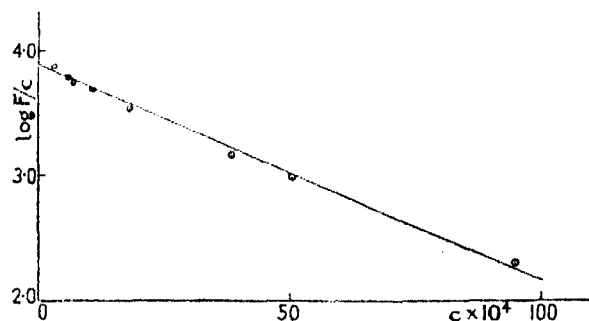


FIG. 3.—CaOPb. $F = Ace^{-nc}$. $n = 390$. $A = 6900$.

In the case of the bismuth solutions, two bands were shown in the direct vision spectroscop, both broad and diffuse, with maxima at about 4600 Å. and 5700 Å. In this case we have from the theory

$$F = A \cdot c \cdot e^{-n_1 c} + B \cdot c \cdot e^{-n_2 c},$$

where n_1 and n_2 refer to the two different centres responsible for the two bands. So that we cannot reduce the relation to a linear form. On plotting F against c (fig. 4) from the observed results, two optima are seen. Taking the values of n_1 and n_2 from this curve and calculating the values of A and B from two different values of F , the values of F according to the theory may be calculated for any value of c . The results of this calculation are shown in Table A. The agreement with the observed values is seen to be very satisfactory.

The experimental evidence thus supports the view that the luminescent centre in solid solutions consists of a definite number of solute molecules

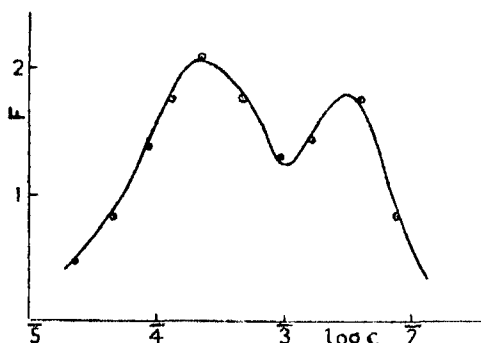


FIG. 4.—CaOBi. $\circ$, observed points; —, calculated curve. $I = Ae^{-n_1c} + Be^{-n_2c}$.
 $A = 2.34 \cdot 10^4$. $B = 1.58 \cdot 10^3$. $n_1 = 5012$. $n_2 = 331$.

associated with one atom or molecule of the activator and that if there are more than one band, each band arises from a different centre.

Table A.—Table showing relation between Intensity of Luminescence and Concentration in the Solid Solution Bi/CaO.

C(atomic) Bi/Ca.	F_1 calcd.	F_2 calcd.	F calcd. $= F_1 + F_2$	F obsd.
0.042279	0.47	0.01	0.48	0.49
0.044617	0.83	0.07	0.90	0.86
0.048576	1.31	0.13	1.44	1.40
0.051342	1.57	0.20	1.77	1.75
0.052233	1.71	0.33	2.04	2.08
0.054638	1.06	0.63	1.69	1.65
0.059376	0.20	1.09	1.29	1.30
0.051606	0.015	1.49	1.50	1.45
0.054000	—	1.70	1.70	1.75
0.057843	—	0.92	0.92	0.88

$$F_1 = 2.34 \times 10^4 C \cdot e^{-5012C}$$

$$F_2 = 1.58 \times 10^3 C \cdot e^{-331C}$$

PART 2.—Liquid Solutions.

There is a large class of substances (notably dyestuffs) which are luminescent in suitable solvents but not in the solid state if pure. The luminescence is, in these cases, obviously an attribute of the state of solution. It was therefore considered interesting to find whether these solutions obey the same law relating brightness and concentration as has been shown to exist for solid solutions.

The solutions chosen for the experimental tests were :—

Uranin ($\text{C}_{20}\text{H}_{10}\text{O}_5\text{Na}_2$) in water.

Fluorescein ($\text{C}_{20}\text{H}_{12}\text{O}_5$) in ethyl alcohol.

Rhodamine 6G ($\text{C}_{28}\text{H}_{27}\text{N}_2\text{O}_3\text{Cl}$) in water.

If the luminescence in the case of these liquid solutions is again due to the existence of an absorbing and re-emitting centre consisting of one molecule of the solute associated with a definite number of solvent molecules, we arrive at the law deduced above

$$F = P \cdot c \cdot e^{-nc} \cdot (1 - e^{-(f_1+f_2)t}) / (f_1 + f_2)$$

for the luminescence emitted on the same side as the exciting light, from a layer of thickness t .

This reduces to the simpler form

$$F = P \cdot c \cdot e^{-nc} \cdot t$$

only if we may write

$$1 - e^{-(f_1+f_2)t} = (f_1 + f_2)t.$$

Now while this simplifying assumption as to the smallness of $(f_1 + f_2)t$ is, for the reasons already given probably justified in the case of luminescent solid solutions, it is neither necessary nor advisable to make the assumption in the present case. For, on the one hand, the absorption coefficients f_1 and f_2 are easily measurable and, on the other hand, they are certainly quite large even for dilutions giving notable luminescence. It was therefore considered advisable to make measurements of the absorption coefficients up to concentrations exceeding that of the optimum.

To determine the absorption coefficient for the exciting light a glass-sided tank T_1 of known thickness t was placed in front of the source and Uviol window. This was followed by a second Uviol screen and another glass-sided tank T_2 containing some of the solution. Observations of the brightness of the luminescence of the solution in tank T_2 when tank T_1 was (a) empty, and (b) filled with the solution under test obviously gives the value of the absorption coefficient for the exciting light for $F_b = F_a \cdot e^{-f_1 t}$.

For the determination of the absorption coefficient for the emitted light a glass-sided tank containing some of the luminescent solution of suitable concentration to act as a source of luminescence by transmission, was placed immediately in front of the Uviol window of the mercury lamp. This was followed by a coloured screen which cut off the remaining exciting light but transmitted the luminescent light. The brightness of the luminescent source

was measured before and after the interposition of a known thickness of the solution under test.

Measurements at different concentrations showed that while the absorption coefficients both for the exciting and emitted light increased with the concentration, the rate of increase is not linear. It has not been possible so far to deduce any simple relation between absorption and concentration. The actual values obtained at the maximum concentrations used were :—

Uranin in water	$f_1 = 3.4 \text{ cm.}^{-1}.$
	$f_2 = 3.8 \text{ cm.}^{-1}.$
Fluorescein in ethyl alcohol	$f_1 = 1.3 \text{ cm.}^{-1}.$
	$f_2 = 5.3 \text{ cm.}^{-1}.$
Rhodamine in water	$f_1 = 4.7 \text{ cm.}^{-1}.$
	$f_2 = 1.8 \text{ cm.}^{-1}.$

These values show that it is necessary to work with very small thicknesses of the solutions if we are to introduce the simplifying approximation

$$1 - e^{-(f_1+f_2)t} = (f_1 + f_2) t.$$

In examining the brightness of luminescence of the solutions at different concentrations, a drop of the solution under test was placed in a shallow circular cavity 0.02 cm. deep and 1 cm. diameter in an ebonite plate and covered over with a thin glass plate to bring the liquid surface flush with the upper edges of the cavity. The directions of observation and illumination were 45° on each side of the normal to the liquid surface ; so that the effective thickness used was $0.02 \times \sqrt{2} \text{ cm.} = 0.028 \text{ cm.}$

Thus the maximum values attained by $(f_1 + f_2)t$ in the three cases were 0.203, 0.185 and 0.181 respectively, so that we may put

$$1 - e^{-(f_1+f_2)t} = (f_1 + f_2) t$$

with a maximum error in the worst case of not more than 2 per cent.

Hence if the theory developed above for solid solutions is applicable to these liquid solutions we have again

$$\begin{aligned} F &= P \cdot c \cdot e^{-nc} \cdot t \\ &= A \cdot ce^{-nc} \quad (t \text{ constant}) \end{aligned}$$

or

$$\log F/c = \log A - (n \log e) c.$$

The results of plotting $\log F/c$ against c from the observations are shown in figs. 5, 6 and 7, together with the values of n deduced from the slope. It will be observed that the linear relation between $\log F/c$ and c to be expected from the theory is again very fairly followed.

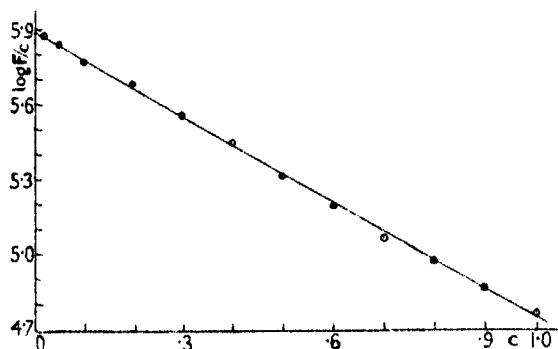


FIG. 5.—Uranin in Water. $n = 1.52 \cdot 10^4$.

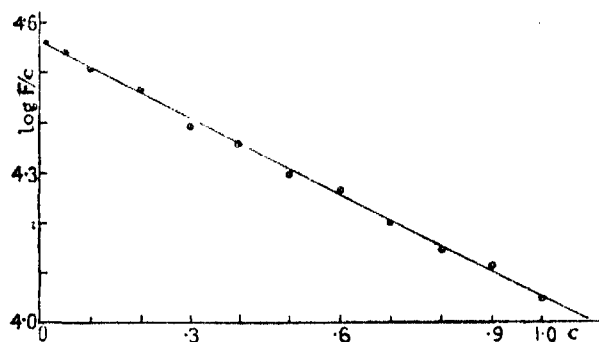


FIG. 6.—Fluorescein in Ethyl Alcohol. $n = 690$.

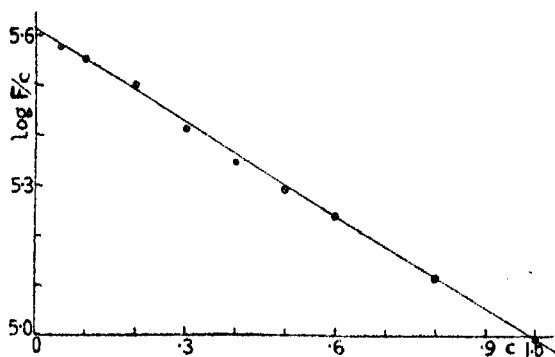


FIG. 7.—Rhodamine in Water. $n = 1.49 \cdot 10^4$.

Thus it appears that the luminescence of liquid solutions, at any rate of this type, can be quantitatively accounted for by the existence of absorbing and re-emitting centres consisting of one molecule of the solute associated with a definite number of solvent molecules.

Further experiments are in progress using the same solute in different solvents with the object of discovering whether any simple relations exist between the size of the centre and the physical properties (*e.g.*, dielectric constant) of the solvent.

The Behaviour of Electrolytes in Mixed Solvents. Part II.—The Effect of Lithium Chloride on the Activities of Water and Alcohol in Mixed Solutions.

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(Communicated by J. Kendall, F.R.S.—Received July 8, 1930.)

In the interaction between ions and solvent molecules, two types of physical effects have been recognised. The first, solvation, may be ascribed, in the absence of definite chemical compound formation between the ions and the solvent, to the attraction exerted by the electric field of the ions on the polarisable molecules of the solvent. Since the elements of a polarisable medium tend to move into those regions where the electric field is greatest, the molecules of water in aqueous salt solutions will tend to congregate round the ions and will be held by quite considerable forces. In the presence of a second substance, having a lower dielectric constant than water, this gives rise to the second or salting-out effect. Since water molecules are attracted by the ions more strongly than those of the other substance, the latter may be displaced or salted-out from the vicinity of the ions and their activity in the solution consequently increased.

This effect has been extensively studied in dilute aqueous solutions* either by means of solubility measurements with sparingly soluble non-electrolytes

* *E.g.*, Setschenow, 'Ann. Chim. Phys.,' vol. 25, p. 226 (1892); Rothmund, 'Z. phys. Chem.,' vol. 33, p. 401 (1900); Glasstone and Pound, 'J. Chem. Soc.,' vol. 127, p. 2660 (1925); Glasstone, Dimond and Jones, *ibid.*, vol. 129, p. 2935 (1926).

or by experiments on the distribution of the non-electrolyte between the aqueous solution and an immiscible solvent in which the electrolyte is not soluble.

The object of the present investigation was to determine the effect of a salt on the activities of both components of a mixed solvent, when the proportion of each component was varied from 0 to 100 per cent. It was hoped that such an investigation would give information as to the relative importance of solvation and salting-out, over the whole range of composition. The substances chosen were water and alcohol, with lithium chloride, one of the few salts which are soluble to a considerable extent in both of these liquids, as the electrolyte.

Experimental.

Method of Experiment.—The partial vapour pressures of alcohol and water in the solutions were determined by the air-bubbling method. This method, which has been extensively used by Perman* for the determination of the vapour pressures of many aqueous solutions and by Foote and Scholes† and Dobson‡ for the determination of the partial pressures of water and ethyl alcohol in mixtures of the two, is probably more accurate than the distillation method of Zawidski§ and is certainly more convenient for determining comparatively small changes produced by a third component.

The method depends on the fact that, if air is bubbled through a solution under conditions such that equilibrium is reached, the quantity of each volatile component present in the vapour is proportional to its partial vapour pressure in the solution. Thus if a volume v of dry air be passed through the solution of water and ethyl alcohol at constant pressure P and temperature T , and if w_1 be the weight of water removed as vapour and w_2 the weight of alcohol removed as vapour, the volume of the water in the saturated vapour is

$$v_1 = w_1 \cdot 22400 (273 + T) \cdot 760/M_1 \cdot 273 \cdot P \text{ c.c.}$$

and the volume of alcohol

$$v_2 = w_2 \cdot 22400 (273 + T) \cdot 760/M_2 \cdot 273 \cdot P \text{ c.c.}$$

where M_1 and M_2 are the molecular weights of water and alcohol. The total volume of the saturated air at temperature T and pressure P is therefore

* 'Proc. Roy. Soc.,' A, vol. 72, p. 72 (1903); 'Trans. Faraday Soc.,' vol. 23, p. 95 (1927).

† 'J. Amer. Chem. Soc.,' vol. 33, p. 1317 (1911).

‡ 'J. Amer. Chem. Soc.,' vol. 127, p. 2871 (1925).

§ 'Z. Phys. Chem.,' vol. 35, p. 129 (1900).

$V + v_1 + v_2$ and if the ideal gas laws are obeyed, according to Dalton's law of partial pressures, the partial pressures of water and alcohol in the vapour are :

$$p_1 = v_1/(V + v_1 + v_2) \cdot P,$$

$$p_2 = v_2/(V + v_1 + v_2) \cdot P.$$

Errors may arise in this calculation for the following reasons—(1) The actual pressure in the bubblers where saturation takes place may be slightly different from the measured atmospheric pressure. In our apparatus the difference was never greater than 1–2 mm. of mercury and was neglected. (2) Water and alcohol dissolve appreciable quantities of air. At 25° the solubility of air is 16.7 c.c. (reduced to N.T.P.) in water* and 110 c.c. in absolute alcohol† per litre. In solutions of lithium chloride the solubilities‡ are probably lower, for it has been shown by Geffken§ among others that the solubility of a gas decreases with increasing salt concentration. Since our solutions were made up in air and a preliminary air bubbling was always carried out, they were certainly saturated with air before the bubbling of the measured volume commenced. (3) The saturated vapours may deviate from the ideal gas laws. According to Dobson (*loc. cit.*) at 25° the deviation of saturated water vapour is about 0.03 per cent. and that of alcohol vapour 0.1 per cent. Perman† also considers that the agreement between the results of the air-bubbling method and distillation methods indicates that the ideal gas law holds with considerable accuracy. (4) The presence of dissolved air affects the molar fractions of the other constituents of the solutions and therefore their partial pressures. In alcohol, the solubility of air corresponds to a total concentration of about 0.005 m., which cannot affect the molar fractions of the other constituents to a significant extent. In other solutions its solubility is smaller.

Preparation of Materials.—Absolute alcohol was prepared as described by Butler and Robertson in the first paper of this series. Lithium chloride was prepared from a Kahlbaum preparation, the chlorine content of which corresponded fairly accurately to $\text{LiCl} \cdot \text{H}_2\text{O}$. It was dissolved in alcohol and filtered to remove any other alkali chlorides present. The greater part of the alcohol in the solution was evaporated at 50° under reduced pressure. The anhydrous lithium chloride which separated on cooling was quickly filtered at the pump and transferred to a flask. It was dried in the manner described

* Seidell, "Solubilities of organic and inorganic substances," p. 19 (1919).

† 'Trans. Faraday Soc.' vol. 24, p. 330 (1928).

‡ Comey, "Dictionary of solubilities," p. 2 (1896).

§ 'Z. Phys. Chem.,' vol. 49, p. 257 (1904).

by Pearce and Hart,* by heating to 170° in a stream of pure dry hydrogen chloride followed by gentle heating in a stream of dry hydrogen until the last traces of hydrochloric acid had been removed. The hydrogen chloride was generated by dropping A.R. sulphuric acid into A.R. hydrochloric acid and was dried by bubbling it through sulphuric acid and then passing it over phosphorus pentoxide in a long inclined tube. The lithium chloride prepared in this way was kept in a vacuum dessicator over phosphorus pentoxide. Its chlorine content as determined by analysis was 83.58 per cent. (LiCl , $\text{Cl} = 83.61$ per cent).

Apparatus.—The apparatus (fig. 1) consisted of three parts having as their functions (a) the measurement of the volume of air used, (b) the complete

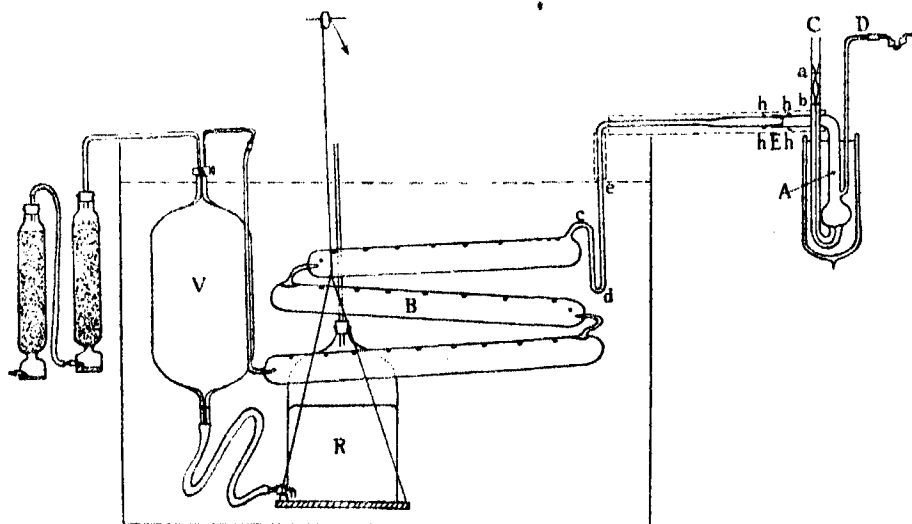


FIG. 1.—Arrangement of Apparatus.

saturation of the air with the vapour of the solution, (c) the determination of the weights of alcohol and water respectively, carried by the measured volume of air.

The measuring vessel *V* was a glass bulb fitted with a capillary two-way tap at the top, by means of which it could be put into connection either with the calcium chloride towers through which air entered or with the bubbler *B*. At its bottom end was a capillary through which connection was made by means of a length of heavy pressure tubing with the mercury reservoir *R*. The capacity of the bulb between the mark on the lower capillary and the upper

* 'J. Amer. Chem. Soc.,' vol. 44, p. 2411 (1922).

tap was determined by weighing the volume of mercury contained between these points. At 12° it contained 10,496.6 gms. of mercury and, taking the density of mercury at this temperature to be 13.5658 gms. per cubic centimeter,* the volume of the vessel is 773.3 c.c. This is the volume of air used in an experiment.

The bubbler B consisted of three inclined tubes fused together, each fitted with a jet to produce a stream of small bubbles of air. Owing to the small inclination of the tubes the bubbles travelled slowly and took from 10 to 15 seconds to pass through the bubbler. Complete saturation of the air was obtained, for the results were found to be reproducible and independent of the rate of passage of air within the range employed. The purpose of the bend *cde*, which did not contain liquid, was to give any spray, which might have been carried over mechanically, an opportunity of settling out. At the point *e* the air is saturated with the vapour of the solution at the temperature of the thermostat. Beyond *e*, the exit tube was kept at a higher temperature than the thermostat by electrically heated mats in order to prevent condensation on the sides of the tube. The capacity of the bubbler was about 200 c.c., so that the small amounts of material removed by evaporation caused no appreciable change in the composition of the solutions.

The total weight of alcohol and water present as vapour in the measured volume of air was 0.1 to 0.2 grams and the determination of their relative proportions presented great difficulty. It was not considered feasible to increase the volume of air so as to permit the collection of a larger quantity of liquid, as this would have greatly increased the time required to carry out each experiment and restricted the range of solutions the partial pressures of which we intended to determine. Among other methods, we tried the combustion of the vapour with red-hot copper oxide and at the surface of a platinum catalyst and the collection of the water vapour and carbon dioxide in suitable absorption tubes. In neither case could we get sufficiently reproducible results, apparently owing to the adsorption of some of the material on the oxidising surfaces. The vapours were next condensed by passing through a tube surrounded by carbon dioxide, and an attempt was made to determine the composition of a thin film of liquid by means of the dipping refractometer with an auxiliary prism. While this was fairly satisfactory in the case of solutions containing a small proportion of alcohol, in the more concentrated solutions the instrument failed to give consistent results, probably owing to the rapid evaporation of the alcohol.

* Landolt-Börnstein Tabellen, 5th ed., p. 77.

In the method finally adopted the collecting tube was fitted with a viscosimeter, by means of which the composition of the small quantity of liquid collected could be determined with sufficient accuracy. From the exit tube of the bubbler the vapour passed into the collecting tube A, which was connected to the former by a tightly fitted ground glass joint without grease of any kind. The two parts of the apparatus were firmly wired together round the glass hooks *h*. The tube A was surrounded by carbon dioxide snow in a Dewar flask, and the condensed vapour collected at its foot. Preliminary experiments in which the air passed through weighed adsorption tubes after leaving A, showed that if the rate of passage of air was sufficiently slow, condensation was complete. In subsequent experiments a small sulphuric acid bubbler was attached to the exit of A to prevent the entry of moisture. The thermostat had plate-glass sides and was electrically controlled. The temperature remained constant to $\pm 0.01^\circ$.

Procedure.—Each solution was made up by weight from absolute alcohol, distilled water and lithium chloride. The bubbler was filled with the solution to be examined, as quickly as possible from a tap funnel, placed in position in the thermostat and attached to the air vessel, which was full of dry air. The heating mats were attached, and a stream of air passed for 10 minutes to ensure that the apparatus contained as much air and vapour in the same state as at the end of the experiment. The tube A was carefully wiped and weighed after standing in the balance case for half-an-hour. It was closed at C (fig. 1) by a piece of rubber tubing fitted with a glass rod, and a small calcium chloride tube was attached at D, so that when carbon dioxide snow was placed round the tube, dry air was sucked in. The preliminary air bubbling was stopped and the tube A attached to the bubbler. The Dewar vessel was slipped into position and filled with carbon dioxide snow. The calcium chloride tube at D was replaced by a small sulphuric acid pulsimeter and the heating mats extended to the bend in tube A.

The vessel V was refilled with dry air, and with its tap in full connection with the calcium chloride towers the level of the mercury was adjusted to an etched line on the capillary at the bottom of V. The tap was now closed and the mercury reservoir raised somewhat. When the air pressure in V had become steady, the tap was opened cautiously and air began to pass through the bubbler. The rate of bubbling was adjusted until one bubble passed through the pulsimeter every 2 seconds. The reason for this slow rate of bubbling was not so much to secure complete saturation of the air, for this is attained much more quickly, but to give the vapour ample time to condense in

A. At the completion of the bubbling mercury just reached the bore of the tap.

The tube A was then disconnected, removed from the Dewar flask, and, after being stoppered at E, allowed to stand for 5 minutes to come to room temperature. It was then closed at all openings and carefully wiped. After standing in the balance case for half-an-hour, the stoppers were removed with as little handling as possible, and the tube weighed.

The tube was then tightly stoppered at E and placed in the thermostat. The liquid was sucked up the fine capillary through a calcium chloride tube attached at C, until the meniscus was above *a* and allowed to flow back. The time taken for the meniscus to move from *a* to *b* was measured with a stop-watch at least 10 times. The viscosimeter had previously been calibrated with solutions containing known percentages of alcohol. The capillary ends in a very flat bulb to reduce to a minimum the variation of the time of flow with the volume of liquid. The time of flow was found to be independent of the quantity of liquid over the range of quantities actually collected.

This method of analysis is quick, the liquid is practically unexposed to the atmosphere and there is very little opportunity for the absorption of moisture and the accuracy, except in the vicinity of the maximum of the viscosity-composition curve, exceeds 0.1 per cent. Two experiments were carried out with each solution.

In solutions containing only 2 and 5 mols. per cent. of water it was desired to find the percentage change in the vapour pressure of water, caused by the presence of the salt, with considerable accuracy and a different method of analysis was employed. The total weight of liquid carried over by the volume *V* of air was determined as above. In order to find the percentage of water, another experiment was carried out, in which 9 to 10 litres of air* were bubbled through the solution by means of an aspirator attached to the collecting tube through a calcium chloride tube (*l*) and by this means 1 to 2 grams of liquid was obtained. The composition of this liquid was determined by means of a Zeiss Industrial Interferometer, which had previously been calibrated with solutions containing known proportions of water. The accuracy with which the composition can be determined in this way is at least 0.01 per cent.

Similar determinations were made with solutions containing 6.4 mols. per cent. alcohol as, owing to the flatness of the viscosity curve in the corresponding region, the accuracy of the viscosity method with these solutions is somewhat low.

* The time taken was about 24 hours.

Experimental Data.—The calibration of the viscosimeter is given in Table I, which gives the mean times of flow of at least two samples of each solution.

Table I.—Calibration of Viscosimeter. Times of Flow of Water-Alcohol Solutions.

Weight per cent. C_2H_5OH .	Time of flow (secs.).	Weight per cent. C_2H_5OH .	Time of flow (secs.).
100	129.8	86	176.8
99	134.8	85	179.4
98	139.5	84	182.1
97	142.5	82	187.8
96	146.1	80	193.4
95	149.4	78	198.8
94	153.0	74	208.4
93	156.2	72	213.3
92	159.4	70	217.6
91	162.8	68	221.5
90	165.9	66	225.6
89	168.7	64	229.5
88	171.4	62	232.6
87	174.0	60	235.4

Table IIa gives in full the experimental figures for 70 per cent. alcohol. N_A is the composition of the solvent, expressed as molecules per cent. ethyl alcohol; m , the molar concentration of lithium chloride (mols. in 1000 grams of solvent), w the total weight of water and alcohol collected in the passage of the measured volume of air, D the weight percentage of alcohol in the liquid collected, P the atmospheric pressure during the experiment and p_w , p_a the calculated partial pressures of water and alcohol in millimetres of mercury.

Table IIa.

N_A .	m .	w .	D° per cent. C_2H_5OH .	P .	p_w .	p_a .	Mean values.	
							p_w .	p_a .
70	0	gm. 0.1009	89.60	mm. 754	mm. 12.94	mm. 43.60	12.95	43.62
	0	0.1010	89.60	754	12.96	43.63		
	0.5	0.1006	90.73	742	11.50	44.04	11.47	44.06
	0.5	0.1007	90.80	744	11.43	44.08		
	1.0	0.0991	91.65	748	10.24	43.90	10.19	43.92
	1.0	0.0991	91.73	742	10.14	43.93		
	4.0	0.1317*	95.00	727	4.18	31.03	4.19	31.13
	4.0	0.1324*	95.00	741	4.20	31.23		

* Volume of air 2V in these experiments.

Table IIb.—Mean Values of Partial Vapour Pressures of Water and Alcohol.

N_a	m	p_w	p_a	N_a	m	p_w	p_a
100	0	0	58.98	70	0	12.95	43.62
	0.5	0	57.21		0.5	11.47	44.06
	1.0	0	54.27		1.0	10.19	43.92
	4.0	0	26.72		4.0	4.19	31.13
98	0	1.141	57.24	50	0	17.24	36.65
	0.5	0.908	55.98		0.5	15.78	37.77
	1.0	0.788	53.78		1.0	14.53	38.13
	4.0	0.277	26.96		4.0	7.65	33.17
95	0	2.286	56.03	25	0	19.48	29.08
	0.5	1.816	54.73		0.5	18.84	30.19
	1.0	1.636	52.69		1.0	18.18	30.90
	4.0	0.580	27.44		4.0	12.70	32.08
90	0	5.381	52.42	6.4	0	21.94	12.29
	0.5	4.547	52.26		0.5	21.65	13.08
	1.0	3.852	50.72		1.0	21.07	13.87
	4.0	1.062	28.21		4.0	16.66	18.01
80	0	9.81	48.04	0	0	23.77	—
	0.5	8.49	47.91		0.5	23.45	—
	1.0	7.33	47.00		1.0	23.05	—
	4.0	2.534	29.65		4.0	19.21	—

The mean values of the partial vapour pressures for the whole series are given in Table IIb. The duplicate determinations rarely differed from each other by more than 5 parts in 1000. Table IIc gives a comparison of our results in water-alcohol solutions containing no lithium chloride (S. and B.), and those obtained from Dobson's data (D.) by graphical interpolation. The agreement is excellent in some cases, but generally our values are somewhat lower.

Table IIc.—Comparison of Observed Vapour Pressures with those obtained from Dobson's Data.

N_A	p_a		p_w	
	D.	S. and B.	D.	S. and B.
0	—	—	23.75	23.77
6.4	12.7	12.29	22.4	21.94
25	29.4	29.08	19.8	19.48
50	37.0	36.65	17.2	17.24
70	44.2	43.62	13.0	12.95
100	59.01	58.99	—	—

The effect of lithium chloride on the partial pressures of water and alcohol in the various solvents is shown in figs. 2 and 3. It can be seen that, while

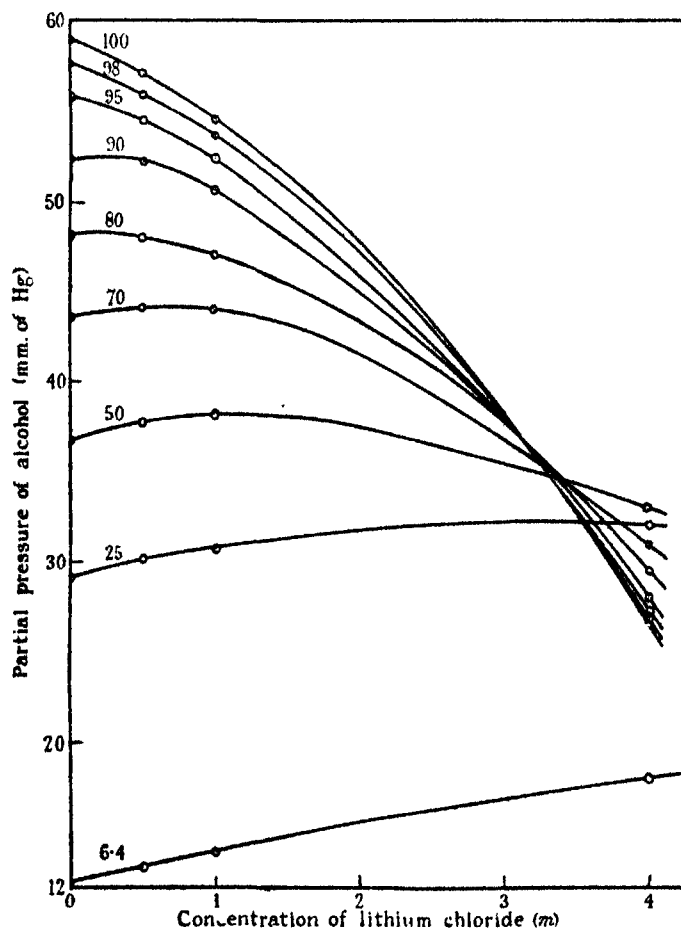


FIG. 2.—Partial Pressures of Alcohol in Water-Alcohol-Lithium Chloride Solutions. (The figures give the molar percentage of alcohol in the solvent.)

increasing concentration of lithium chloride causes a decrease in the partial pressure of water in all solutions, its effect on the alcohol varies with the composition of the solvent. In solutions containing a large proportion of alcohol, its partial pressure falls steadily as the lithium chloride concentration increases, and in the solution containing 6.4 mols. per cent. alcohol it rises steadily, while in intermediate solutions it first rises and then falls.

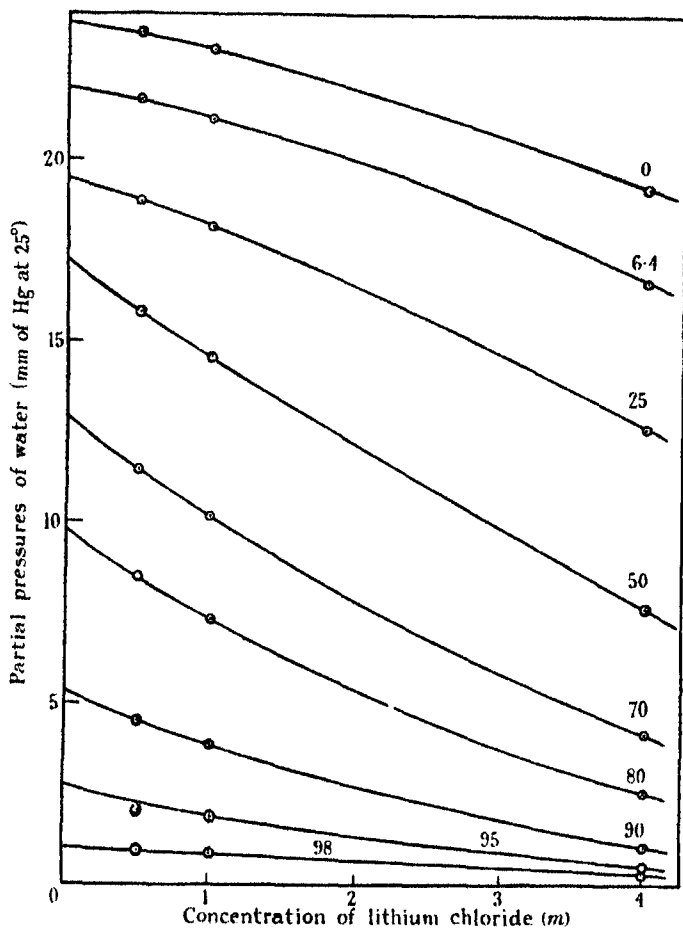


FIG. 3.—Partial Pressures of Water in Water-Alcohol-Lithium Chloride Solutions. (The figures give the molar percentage of alcohol in the solvent.)

Activities and Relative Activities of Water and Alcohol.—Assuming that the vapour obeys the ideal gas law, the activity of alcohol in a solution is given by

$$\alpha_a = p_a/p_a^0,$$

where p_a is the partial pressure of alcohol over the solution and p_a^0 vapour pressure of pure alcohol at the same temperature. Similarly the activity of water is $\alpha_w = p_w/p_w^0$. In order to state concisely the effect of lithium chloride on activities in the solutions, we shall call α_a/α_a^0 , where α_a^0 is the activity of alcohol in a given mixture of alcohol and water and α_a its activity in the same solvent containing lithium chloride, the *relative activity* of alcohol in this solution. Similarly α_w/α_w^0 is the relative activity of water in a solution.

Table III gives the activities and relative activities of water and alcohol in the solutions. The relative activities of water and alcohol are shown in figs. 4 and 5.

Table III.—Activities and Relative Activities of Water and Alcohol in Lithium Chloride Solutions at 25°.

N_A	m	a_a	a_w	a_a/a_a^0	a_w/a_w^0
100	0	1.000	—	1.000	—
	0.5	0.9699	—	0.9699	—
	1.0	0.9202	—	0.9202	—
	4.0	0.453	—	0.453	—
98	0	0.9764	0.04806	1.000	1.000
	0.5	0.9497	0.0383	0.9725	0.795
	1.0	0.9118	0.0331	0.934	0.690
	4.0	0.4573	0.0116	0.468	0.2425
95	0	0.9504	0.0962	1.000	1.000
	0.5	0.9286	0.0764	0.977	0.794
	1.0	0.8940	0.0688	0.9405	0.7155
	4.0	0.4654	0.0244	0.490	0.254
90	0	0.8900	0.2264	1.000	1.000
	0.5	0.8874	0.1914	0.998	0.845
	1.0	0.8611	0.1621	0.9685	0.716
	4.0	0.4786	0.0446	0.538	0.197
80	0	0.8155	0.4130	1.000	1.000
	0.5	0.8133	0.3573	0.998	0.865
	1.0	0.7980	0.3085	0.970	0.747
	4.0	0.5033	0.1066	0.6175	0.258
70	0	0.7404	0.5575	1.000	1.000
	0.5	0.7481	0.4829	1.011	0.866
	1.0	0.7457	0.4282	1.008	0.768
	4.0	0.5286	0.1763	0.714	0.315
50	0	0.6223	0.7253	1.000	1.000
	0.5	0.6410	0.6639	1.030	0.915
	1.0	0.6473	0.6114	1.040	0.843
	4.0	0.5631	0.3219	0.902	0.444
25	0	0.4938	0.8195	1.000	1.000
	0.5	0.5126	0.7928	1.038	0.967
	1.0	0.5247	0.7649	1.063	0.933
	4.0	0.5446	0.5344	1.132	0.652
6.4	0	0.2083	0.9230	1.000	1.000
	0.5	0.2217	0.9110	1.064	0.987
	1.0	0.2352	0.8864	1.129	0.960
	4.0	0.3054	0.7010	1.465	0.760
0	0	—	1.000	—	1.000
	0.5	—	0.9865	—	0.9865
	1.0	—	0.9696	—	0.9695
	4.0	—	0.8081	—	0.808

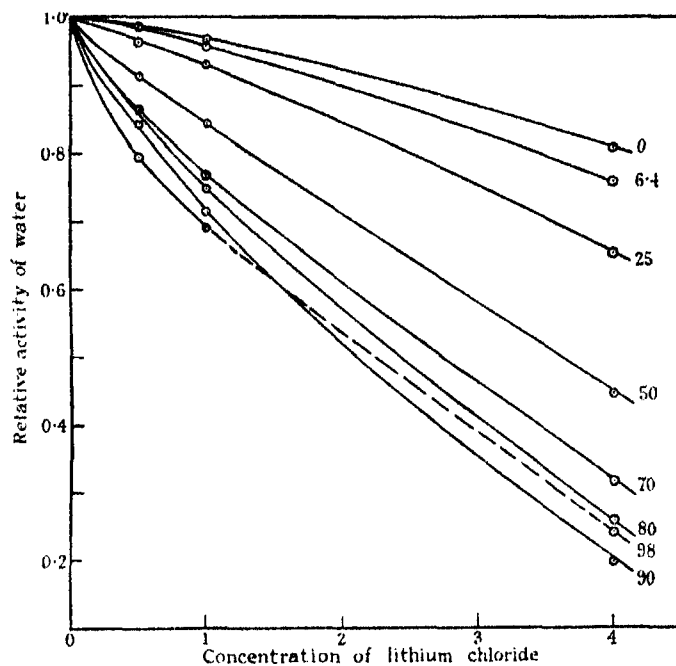


FIG. 4.—Relative Activities of Water in Water-Alcohol-Lithium Chloride Solutions.

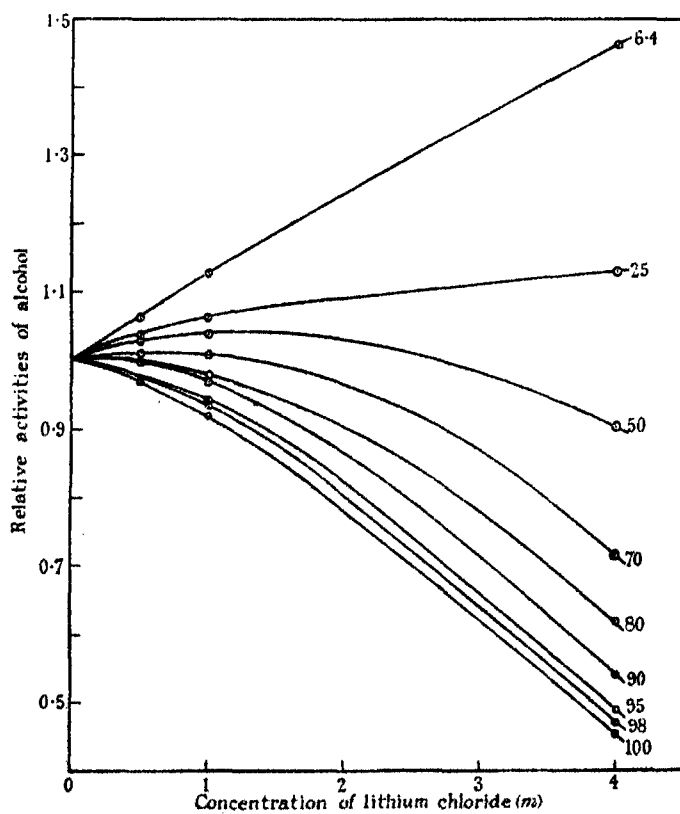


FIG. 5.—Relative Activities of Alcohol in Water-Alcohol-Lithium Chloride Solutions.

Discussion.

The effect of certain non-electrolytes on the partial vapour pressures of a solution containing 38 per cent. (by weight) of alcohol in water, has been investigated by Wright,* who correlated the effects observed with the solubility of the non-electrolyte in the two components of the solvent. He found that, when the added substance was soluble in water but not in alcohol, and when it was soluble in both liquids, it raised the vapour pressure of alcohol and lowered that of water; when it was soluble in alcohol only, it usually lowered the vapour pressure of alcohol and slightly raised that of water. In a later paper† he studied the effect of various salts, at the concentration 0.5 *m.*, on the partial pressures of a solution containing 10 mols. per cent. alcohol in water and found, in agreement with his previous work, that the vapour pressure of alcohol was always raised while that of water was lowered.

The present investigation shows, however, that the effects produced by adding an electrolyte to a mixed solvent vary according to the composition of the latter.

The activity of water is lowered by the addition of lithium chloride in all solutions, and in solutions containing from 100 to 80 mols. per cent. alcohol the activity of alcohol is similarly affected. In solutions containing 50 to 70 mols. per cent. alcohol, concentrations of 0.5 *m.* and 1.0 *m.* lithium chloride cause an increase in its activity, while increasing the lithium chloride concentration to 4 *m.* causes a subsequent decrease. In solutions containing 0 to 25 mols. per cent. alcohol, the activity of alcohol is raised by all concentrations of lithium chloride.

These effects are readily accounted for qualitatively in terms of the relative attractions of the ions for the two types of solvent molecules. Since the more polar molecules of a solution tend to congregate where the electric field is strongest, we should expect to find in the immediate vicinity of the ions a greater proportion of water molecules than in the bulk of the solution. The activity of water should accordingly be lowered in all solvents, and we should expect the lowering to be greater the smaller the proportion of water, since a greater part of the water present in the solution will be attached to the ions.

It is evident from Table III that the relative activity of the water is reduced to a greater extent by lithium chloride as the proportion of water decreases. The only exceptions are the solutions of 4 *m.* lithium chloride in 95 and 98 per

* 'J. Chem. Soc.,' vol. 121, p. 2251 (1922); vol. 123, p. 2493 (1923).

† 'J. Chem. Soc.,' vol. 125, p. 2068 (1924).

cent. alcohol, in which we find that the fractional lowering of the water pressure is less than in the corresponding 90 per cent. alcohol solution. This abnormality may, however, be due to the great difficulty of determining accurately the effect of lithium chloride on the very small vapour pressure of water in these solutions. These two points are also present anomalies in the relationship shown in fig. 6.

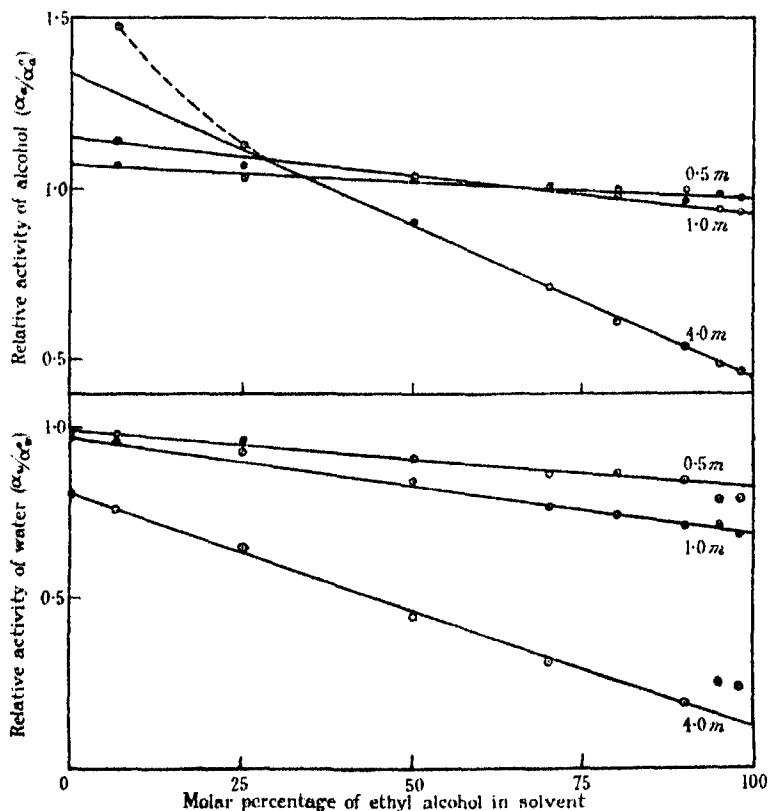


FIG. 6.—Variation of Relative Activities of Alcohol and Water with Molar Fraction of Alcohol in Solvent at constant Lithium Chloride Concentration.

At the beginning of this investigation we thought it probable that, in solutions containing only a small proportion of water and a large amount of lithium chloride most of the water would be firmly attached to the ions and its activity reduced almost to zero. This, however, is not the case. The activity of water, even in the solution containing 0.17 mols. of water per 1000 grams is only reduced to 25 per cent. of its original value by 4 m. lithium chloride. In these solutions the activity of alcohol is considerably lowered

by lithium chloride and the ions are probably largely solvated by alcohol molecules. It appears, therefore, that when only a small proportion of water molecules is present, the large excess of alcohol molecules partially compensates for the superior attraction of the ions for water molecules and prevents them being completely taken up by the ions. The behaviour of alcohol (fig. 5 and Table IV) is also in accordance with this conception. In alcohol-rich solutions its activity is lowered by the addition of lithium chloride, but the lowering diminishes as the proportion of water increases until an effect in the opposite direction appears at low concentrations of lithium chloride and spreads, in greater proportions of water, to the higher concentrations. We may suppose that the ions are largely solvated by alcohol molecules when only a small proportion of water is present. As the solvent becomes richer in water, the latter has a better chance of entering the electric fields of the ions and its greater polarisability as compared with alcohol soon makes itself felt by excluding alcohol molecules from this region to an increasingly greater extent. This "salting out" effect becomes predominant over the "solvation" effect, first at low lithium chloride concentrations, and finally, when only 25 mols. per cent. of alcohol is present, over the whole curve.

In fig. 6 values of α_w/α_w^0 and α_a/α_a^0 for each concentration of lithium chloride are plotted against N_a , the molar fraction of alcohol in the solvent. It is evident that, at constant concentration of lithium chloride, the relative activities of both water and alcohol are nearly linear functions of the molar fraction of alcohol in the solvent. The only considerable deviation is that of alcohol in a 6.4 mol. per cent. solution containing 4 m. lithium chloride. With this exception the results can be expressed by the equations :

$$\alpha_a/\alpha_a^0 = 1 + N_a \cdot f_a(m) + N_w \cdot f_a'(m) \quad (1)$$

$$\alpha_w/\alpha_w^0 = 1 + N_w \cdot f_w(m) + N_a \cdot f_w'(m) \quad (2)$$

where $f_a(m)$ and $f_w(m)$ are functions of the salt concentration, representing its effect on pure water and pure alcohol respectively, and $f_a'(m)$ and $f_w'(m)$ are also functions of the salt concentration, which represent the changes in the relative activities of alcohol and water produced by the addition of water and alcohol, respectively.

The values of these functions for the three concentrations of lithium chloride employed are given in Table V. Thus, in the presence of 0.1 lithium chloride the equations become :

$$\alpha_a/\alpha_a^0 = 1 - 0.0007 N_a + 0.0015 N_w$$

$$\alpha_w/\alpha_w^0 = 1 - 0.0003 N_w - 0.0031 N_a.$$

Table V.

	0.5 <i>m</i> .	1.0 <i>m</i> .	4.0 <i>m</i> .
$f_a(m)$	-0.0003	-0.0007	-0.0055
$f_a'(m)$	+0.00075	+0.0015	+0.0034
$f_w(m)$	-0.0001	-0.0003	-0.0019
$f_w'(m)$	-0.0017	-0.0031	-0.0088

Within the limits of agreement of the data with the above equations, the effects of lithium chloride on the activities of water and alcohol are completely summed up in fig. 7, in which the functions $f_a(m)$, $f_a'(m)$, $f_w(m)$ and $f_w'(m)$

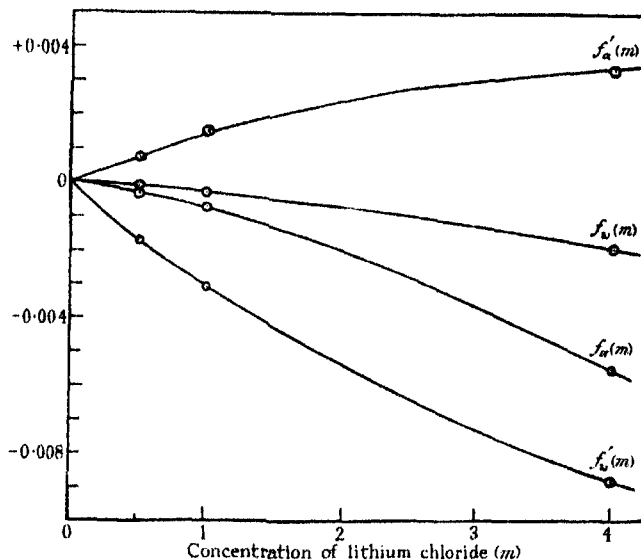


FIG. 7.—Variation of the Functions $f_a(m)$, $f_a'(m)$, $f_w(m)$ and $f_w'(m)$ with Salt Concentration.

are plotted against the salt concentrations. Thus, the curves of $f_a(m)$ and $f_a'(m)$ represent the effect of the salt on the relative activities of alcohol in 100 per cent. alcohol and 100 per cent. water respectively, and the curve of the relative activity of alcohol in a mixed solvent lies between these curves, its position being determined by the molar fractions of alcohol and water in the solvent according to the simple mixture rule. $f_w(m)$ and $f_w'(m)$ similarly represent the effect of the salt on the relative activities of water in 100 per cent. water and 100 per cent. alcohol, and the same rule applies to mixed solvents.

According to (1) the relative activity of alcohol, which is usually taken as

a measure of the salting-out effect, is a function of the molar fractions of alcohol and water in the solution. Measurements of the salting-out effect have hitherto been made exclusively in dilute aqueous solutions, in which the molar fraction of water remains nearly 1, and the part played by the molar fractions of the non-electrolyte has escaped notice. We have seen that the behaviour of alcohol can be represented by two terms, the first of which, $N_a \cdot f_a(m)$, is due to the solvation of the ions by alcohol, and the second, $N_w \cdot f'_a(m)$, to the salting-out or displacement of alcohol molecules round the ions by water molecules. This second term can be taken as a measure of the true salting-out effect, and $f'_a(m)$, which has nearly the same value in all mixtures, with the exception of solutions containing a large quantity of salt and a small proportion of alcohol, can be regarded as the *salting-out constant* for the concentration m of lithium chloride.

Summary.

1. An air-bubbling method has been devised for the determination of the partial pressures of water and alcohol in mixed solutions, in which the volume of air required is less than 2 litres.

2. Measurements have been made at 25° of the partial vapour pressures of water-alcohol solutions containing from 0 to 100 per cent. of alcohol and lithium chloride at concentrations 0.0 m., 0.5 m., 1.0 m. and 4.0 m.

3. It has been found that lithium chloride in water-alcohol solutions lowers the activity of water, while it may either lower or raise that of alcohol, according to the composition of the solvent and the concentration of lithium chloride. The fractional lowering of the vapour pressure of water is always greater than that of alcohol.

4. An approximately linear relationship has been established between the relative activities of both water and alcohol and the molar fraction of alcohol in the solvent, at constant lithium chloride concentration.

5. It is possible to distinguish approximately the effects of the solvation of ions by alcohol molecules and the salting-out of alcohol by the interaction of the ions and water.

We wish to express our indebtedness to Imperial Chemical Industries, Ltd., for a grant which enabled us to purchase the dipping refractometer and to the Moray Research Fund of the University of Edinburgh for a grant for the purchase of the interferometer. One of us (J.A.V.B.) has also to acknowledge a Carnegie Teaching Fellowship, held during part of the period occupied by the research.

*Colorimetric Investigations of Indicators in presence of
Neutral Salts.*

By N. V. SIDGWICK, F.R.S., W. J. WORBOYS and L. A. WOODWARD.

(Received July 30, 1930.)

It is known that the colour exhibited by a definite concentration of an indicator in a solution of given hydrogen ion concentration is changed by the presence of neutral salts.* As is shown in the present paper, the evaluation of this neutral salt effect by colorimetric measurements can be made to furnish information as to the dissociation of the indicator in salt solutions, and, further, the knowledge so obtained can be used to investigate the dissociation of other substances in presence of neutral salts. The colorimetric method employed was similar to that of v. Halban and Geigel,† making use of the photoelectric effect. The advantages of this over the photographic method have recently been discussed by v. Halban and Eisenbrand.‡ Our apparatus enabled the absorption of a solution to be measured against that of an optical wedge, so that the photoelectric effect entered only as a null-point observation.

I. *The Colorimeter.*

A parallel beam of white light passes through a glass cell containing the solution to be measured, and then through a glass prism. The light of a narrow wave-length band is admitted to the photoelectric cell through a slit, before which an optical wedge is placed. The photoelectric current passes to earth through a fixed resistance, and gives a steady deflection to the needle of a sensitive electrometer. The cell and solution are then removed, and the wedge is shifted so as to absorb more light, until the original electrometer deflection is restored. The absorption corresponding to the wedge shift is then equal to that of the cell and solution.

For a homogeneous medium of thickness d the law of absorption states that $\log I/I_0 = kd$, where I and I_0 are the emergent and incident intensities, and k is a constant. The thickness of the wedge varies linearly with the distance measured along it, and hence the values of $\log I/I_0$ do so too. With the

* See for example Szyskowski, 'Z. Phys. Chem.,' vol. 58, p. 420 (1907); vol. 73, p. 269 (1910); vol. 78, p. 426 (1911); vol. 84, p. 91 (1913).

† 'Z. Phys. Chem.,' vol. 96, p. 214 (1920).

‡ 'Proc. Roy. Soc.,' A, vol. 116, p. 153 (1927).

coloured solution in the cell the thickness is constant, but the concentration x of the coloured molecular species is variable, and by Beer's law $\log I/I_0 = k' \times x$. We shall call this function $\log I/I_0$ the "colour" c of the solution; and it will be seen that, in the comparison method described above, "colours" are measured directly by the lateral wedge shift expressed in centimetres. The method has the advantage that it is not necessary to calibrate the electrometer, or to know the value of the photoelectric current.

As this apparatus was subsequently replaced by a more convenient "flicker" form (see the following paper), it can be briefly described. The light source was a 36-watt gas-filled filament lamp, which was kept sufficiently steady by means of a floating battery of accumulators inserted in parallel with the laboratory mains. The prism had a face 4 inches by 3 inches; the spectrum, of which the visible part was about 5.5 cm. long, was focussed by a 3-inch lens on the adjustable slit of a wooden box containing the photoelectric cell; this box could be moved at right angles to the incident light, so as to select any desired spectral band. The optical wedge was arranged just in front of the box so as to move transversely in the beam; its position could be read off on a suitable scale. The absorption cell, which was made of glass with accurately parallel faces 1 cm. apart, was inserted normally in the parallel portion of the beam.

A rubidium photoelectric cell was used, as this metal has its maximum sensitivity in the wave-length region examined, *i.e.*, about 4850 Å.U. This was obtained from Prof. Lindemann. The metal was charged negatively to about 200–300 volts, and the ring terminal connected to the needle of a Lindemann-Keeley electrometer,* which was mounted on the stage of a microscope, and had its plates connected with an adjustable battery. This instrument is very sensitive, and has the advantage of a very short period. The ring terminal of the cell was also connected to earth through a fixed leak of high resistance, consisting of a U-tube filled with a mixture of xylene and alcohol. An earthing switch for the cell was also provided, specially designed so as to work without friction, in order not to affect the electrometer. The electrometer, leak and switch, with their wiring, were enclosed in an earthed metal box, and the box containing the cell was coated with tinfoil. The whole apparatus was set up and used in a dark room.

* 'Phil. Mag.,' vol. 47, p. 577 (1924).

II. Experiments with Methyl Orange.

Theory of the Colour Changes.—Methyl orange is the sodium salt of *p*-dimethylamino-azo-benzene *p*-sulphonic acid. In neutral or alkaline solution its colour is yellow, and changes to red when the solution is made acid. There is a tautomeric change from the true acidic form, which we may write XOH, to the pseudo-acidic HXO, so that in solution we have an equilibrium



The colour change is due to the tautomeric change; but since the amount of XOH is small, and is always proportional to that of HXO, we may conveniently regard the colour as proportional to the ionisation, as in Ostwald's original theory.

Since methyl orange contains a dimethylamino-group, it is an amphoteric electrolyte; but Tizard has shown* that the basic dissociation is so small that it may be neglected.

Following Tizard we will define the unit of colour as the "colour" (itself defined as in Section I) of a slightly alkaline solution of methyl orange at a given concentration; here, of course, the indicator is wholly in the ionised state. Further, we will define the relative colour of any other solution (with the same indicator concentration) as the ratio of its colour to the unit colour. In a solution containing excess of a strong acid the indicator will be wholly undissociated; the relative colour of this solution is called c_1 . All the values of the colour c must lie between c_1 and unity. If, when the hydrogen-ion concentration of the solution is $[\text{H}]$, the fraction y of the indicator is undissociated, the relative colour is given by the simple additive expression

$$c = c_1 y + (1 - y). \quad (1)$$

Also if K is the apparent dissociation constant of the indicator acid, then

$$K = [\text{H}](1 - y)/y. \quad (2)$$

Eliminating y between (1) and (2) we obtain the Tizard relation

$$K = [\text{H}](c_1 - c)/(c - 1). \quad (3)$$

This equation may be used for the experimental determination of K by means of colour measurements at known values of $[\text{H}]$. A convenient method is to use known amounts of hydrochloric acid; but Tizard has pointed out (*loc. cit.*) that the concentration $[\text{H}]$ of free hydrogen ion is less than that of the acid employed, because part of the hydrogen ions has combined with the indicator

* 'J. Chem. Soc.,' vol. 97, p. 2480 (1910).

anions to form red undissociated molecules of indicator acid. This may be allowed for as follows. If the dilution of the indicator be v , then by (1) the concentration of the undissociated part is

$$\frac{y}{v} = \frac{c-1}{c_1-1} \times \frac{1}{v}. \quad (4)$$

This is equal to the concentration of the combined hydrogen-ion [H bound]. The value of the free [H] which must be used in equation (3) is therefore given by

$$[H_{\text{free}}] = [H_{\text{total}}] - [H_{\text{bound}}] = [\text{HCl}] - \frac{c-1}{c_1-1} \times \frac{1}{v}. \quad (5)$$

where [HCl] is the total concentration of acid used.

Measurement of K for Methyl Orange in absence of Neutral Salts.

The maxima of the absorption bands of the yellow and red forms of methyl orange lie respectively at about 4650 and 5050 Å.U., whilst at about 4690 Å.U. the absorption curves cut one another. It was found empirically that the best results were obtained at a point where the value of the relative colour c_1 , of the red (acid) solution lay between 2.5 and 3.0. The apparatus did not allow of exact measurement of the wave-length; the position of the cell was chosen so as to give a value of c_1 between the above limits. The light formed a band about 10 Å.U. wide, with a wave-length of about 4850 Å.U.

An N/2000 solution of Kahlbaum's methyl orange (carefully dried) was made up, and 200 c.c. of this diluted to 21, to give the stock solution of strength N/20,000. All solutions were made up with conductivity water, and after removal of dust by filtration were stored in durosil flasks. For each determination 50 c.c. of the stock solution were made up to 100 c.c. with the necessary amount of acid and water. Thus the indicator was N/40,000; the acid varied from N/20 to N/10,000. The solution was put in the cell (1 cm. thick) and measured as described above. The temperature was that of the dark room, which was $18^\circ \pm 0.5^\circ$. Each determination was repeated several times with fresh solutions, and the maximum error in the value of c was less than 1 per cent. The results are given in Table I. The first column gives the concentration of the acid used; the values in the third column are calculated by equation (4), using $v = 40,000$. The fourth is the difference between the first and third; the last column gives the dissociation constant of the indicator from equation (3).

Table I.

[HCl] $\times 10^4$.	c (obs.).	[H _{bound}] $\times 10^4$.	[H _{free}] $\times 10^4$.	K $\times 10^4$.
196.8	2.76	0.25	196.55	—
98.5	2.76	0.25	98.25	—
49.2	2.66	0.24	49.0	2.95
19.68	2.52	0.22	19.46	3.07
9.85	2.34	0.19	9.66	3.03
4.92	2.08	0.15	4.77	3.00
1.968	1.67	0.095	1.873	3.05
0.985	1.40	0.057	0.928	3.16
0.492	1.23	0.033	0.459	3.06
0.1968	1.07	0.0090	0.1869	(4.51)
0.0985	1.03	0.0043	0.0942	(5.43)

In the first two acid concentrations there is excess of acid, and hence $c = c_1 (= 2.76)$. For lower values of [HCl], K remains reasonably constant except in the two most dilute solutions: in these a large error is to be expected, partly from the greater effect of impurities, and also because the value of $(c_1 - c)/(c - 1)$ in equation (3) changes very rapidly when c becomes nearly equal to unity (dilute acid) or nearly equal to c_1 (strong acid).

The mean value of K is 3.03×10^{-4} at 18° . Interpolation from the results obtained by Tizard* with a Donnan tintometer at different temperatures gives for 18° the value 3.0×10^{-4} . After these measurements were finished, Güntelberg and Schiödt† obtained a rather higher value, 3.23×10^{-4} , which our later measurements with a more accurate apparatus (see following paper) tend to confirm.

Measurements with Methyl Orange in Presence of Neutral Salts.

Since at the dilutions used the hydrochloric acid may be taken to be completely dissociated, the colour change caused by the presence of a neutral salt in an acid solution of methyl orange must be due to one or both of two different causes: (1) the neutral salt may alter the absorption bands of the coloured forms of the indicator, and (2) it may affect the chemical equilibrium between these forms.

The first possibility can be studied independently of the second if we deal with solutions in which the indicator is either completely in the yellow or completely in the red form. There can be no change in their equilibrium, and

* *Loc. cit.*, and 'J. Chem. Soc.', vol. 117, p. 150 (1920).

† 'Z. Physikal. Chem.', vol. 135, p. 393 (1928).

the colour change produced by the neutral salt must be due to a change in the absorption of the two forms.

The measurements were made with N/40,000 methyl orange containing either one drop of N/2 potassium hydroxide or 10 c.c. of N hydrochloric acid to 100 c.c. The salts used were sodium chloride, bromide, chlorate and nitrate, and potassium chloride and bromide. The purest B.D.H. salts were recrystallised from water, except the sodium chloride, which was recrystallised from water by addition of alcohol. They were carefully dried. Conductivity water was used throughout.

At the concentrations examined (N/1000 to 3N) the salts themselves (in the absence of an indicator) gave no measurable absorption. Below N/2 the colour change produced in the indicator was negligible; at higher concentrations a slight increase of colour was observed which seemed to be the same for all salts examined; but it was so small that individual differences might well escape notice. The mean values are given in Table II, the second and third columns giving the observed colours of the slightly alkaline (100 per cent. yellow form) and excess acid (100 per cent. red form) solutions, referred to the colour of the alkaline solution in the absence of salt as unity. In the last column are the values of c_1 referred to the alkaline colour in the absence of salt; it will be seen that these are practically constant, the yellow and red colours being increased to the same extent.

Table II.—Effect of Salts on Absorption of Methyl Orange.

Salt concentration.	Alkaline relative colour.	c_1 relative to unity.	c_1 relative to alkaline colour.
0.0 N	1.00	2.52	2.52
0.5	1.007	2.555	2.53
1.0	1.029	2.592	2.53
2.0	1.052	2.667	2.53
3.0	1.077	2.740	2.54

When using equation (3) for solutions containing neutral salt, the values of c and c_1 employed must be referred to the alkaline colour at the same concentration of the salt. The effect on the absorption of the indicator forms is then entirely eliminated. This procedure is adopted in all subsequent calculations.

This effect is, however, far too small to account for the whole colour change

produced when a neutral salt is added to an acidified solution of methyl orange in which both yellow and red forms are present. The bulk of this change must be due to the second salt effect, a change in the equilibrium of the coloured forms. Modern views of activity lead us to expect that the value of the classical dissociation constant of a weak acid will be affected by the presence of neutral salts.

A series of measurements was therefore made, by the method described above, of the dissociation constant of methyl orange in presence of varying concentrations of several salts. The concentration of hydrochloric acid was always so small that it could be regarded as wholly dissociated. The indicator was N/40,000, and the temperature $18^{\circ} \pm 0.5^{\circ}$. Each determination was made twice with fresh solutions, and concordant results were obtained. Up to N/10 all the salts used (NaCl, NaBr, NaClO₃, NaNO₃, KCl, KBr) caused the same colour change within the limits of experimental error. The results for sodium chloride are given in Table III, and those for the other salts at higher

Table III.—Methyl Orange + HCl + Sodium Chloride.

Salt concentration.	<i>c</i> (obs.).	[H _{bound}] × 10 ⁴ .	[H _{free}] × 10 ⁴ .	K × 10 ⁴ .
0.0 N	1.55	0.09	1.72	(3.03)
0.001	1.54	0.09	1.72	3.12
0.01	1.51	0.08	1.73	3.43
0.05	1.48	0.08	1.73	3.75
0.1	1.48	0.08	1.73	3.75
0.5	1.57	0.09	1.72	2.86
1.0	1.70	0.11	1.70	1.99
2.0	1.97	0.16	1.65	0.935
3.0	2.16	0.19	1.62	0.502

concentrations in Table IV. The values obtained for sodium chlorate and nitrate were identical. In these tables the second column gives the value of *c* referred to the alkaline colour at that particular salt concentration as unity. The values of [H_{bound}] are given by equation (4), using an observed value of *c*₁ = 2.52 at all concentrations.* The value of [H_{free}] in absence of salt (1.72) was calculated by equation (3) for K = 3.03 × 10⁻⁴, so that in absence of salt

$$[\text{H}_{\text{total}}] = (1.72 + 0.09) \times 10^{-4} = 1.81 \times 10^{-4}.$$

* It is to be noticed that small differences in the value of *c*₁ in different sets of measurements only indicate slight differences in the wave-length of the light used, i.e., in the setting of the apparatus; since the value of *c*₁ used was in every case obtained experimentally for the particular set of measurements, no error is produced in the results.

Table IV.—Methyl Orange + HCl + Neutral Salts.

Salt.	Salt concentration	c (obs.).	$[H_{\text{bound}}] \times 10^4$.	$[H_{\text{free}}] \times 10^4$.	$K \times 10^4$.
Potassium chloride	0.5 N	1.56	0.09	1.72	2.95
	1.0	1.64	0.11	1.70	2.34
	2.0	1.82	0.13	1.68	1.43
	3.0	1.98	0.16	1.65	0.91
Sodium bromide	0.5 N	1.57	0.09	1.72	2.86
	1.0	1.73	0.12	1.69	1.83
	2.0	2.02	0.17	1.64	0.805
	3.0	2.22	0.20	1.61	0.396
Potassium bromide	0.5 N	1.57	0.09	1.72	2.86
	1.0	1.69	0.11	1.70	2.04
	2.0	1.95	0.16	1.65	0.99
	3.0	2.12	0.18	1.63	0.582
Sodium nitrate and sodium chlorate	0.5 N	1.57	0.09	1.72	2.86
	1.0	1.68	0.11	1.70	2.10
	2.0	1.89	0.15	1.66	1.17
	3.0	2.06	0.17	1.64	0.712

The values of $[H_{\text{free}}]$ in presence of salt (column 4) are then given by

$$[H_{\text{free}}] = 1.81 \times 10^{-4} - [H_{\text{bound}}].$$

This method of calculation eliminates any possible error due to traces of free acid or alkali in the salts used.

It will be seen from Table III that the value of K rises to a maximum (25 per cent. above that for pure water) between $N/20$ and $N/10$; and subsequently falls to a much lower point than that at which it started. This is in agreement with the recent determinations of Güntelberg and Schiödt (*loc. cit.*).

The knowledge of K for a given salt concentration enables us to investigate the dissociation of other acids under the same conditions; for by using the proper value of K in equation (3) we can calculate true hydrogen-ion concentrations in salt solutions from the colour measurements. As an example a series of measurements were carried out with a constant amount of an acetic acid-ammonia buffer in place of hydrochloric acid. The indicator concentration was $N/53,000$, and the solutions were made up as before. The results are given in Tables V and VI. Temperature 18° .

Here again all the salts gave the same effect up to $N/10$; the lower concentrations are given only in Table V for sodium chloride. The values of c are in terms of the alkaline colour at the same salt concentration. The values of $[H_{\text{free}}]$ are calculated from (3) using the observed value of $c_1 = 2.58$, and employing in each case the appropriate value of K from Table III.

Table V.—Methyl Orange + Buffer + Sodium Chloride.

Salt concentration.	<i>c</i> (obs.).	[H _{free}] × 10 ⁴ .
0.00 N	1.54	1.58
0.001	1.56	1.71
0.01	1.57	1.88
0.05	1.59	2.24
0.1	1.62	2.42
0.5	1.82	3.08
1.0	1.91	2.70
2.0	2.10	2.14
3.0	2.25	1.90

Table VI.—Methyl Orange + Buffer + Neutral Salts.

Salt.	Salt concentration.	<i>c</i> (obs.).	[H _{free}] × 10 ⁴ .
Potassium chloride	0.5 N	1.78	2.88
	1.0	1.83	2.59
	2.0	1.94	2.10
	3.0	2.01	1.61
Sodium bromide	0.5 N	1.92	2.99
	1.0	2.04	2.52
	2.0	2.20	2.54
	3.0	2.32	2.01
Potassium bromide	0.5 N	1.81	3.01
	1.0	1.90	2.70
	2.0	2.06	2.02
	3.0	2.10	1.78
Sodium nitrate and sodium chlorate	0.5 N	1.81	3.01
	1.0	1.88	2.64
	2.0	2.02	2.13
	3.0	2.14	1.84

The results are of the same type for all salts; the value of [H_{free}] rises with increase of salt concentration, and passes through a maximum at about N/2.

III. Discussion of Results.

For a weak electrolyte, such as a uni-univalent organic acid HA, the equilibrium relations

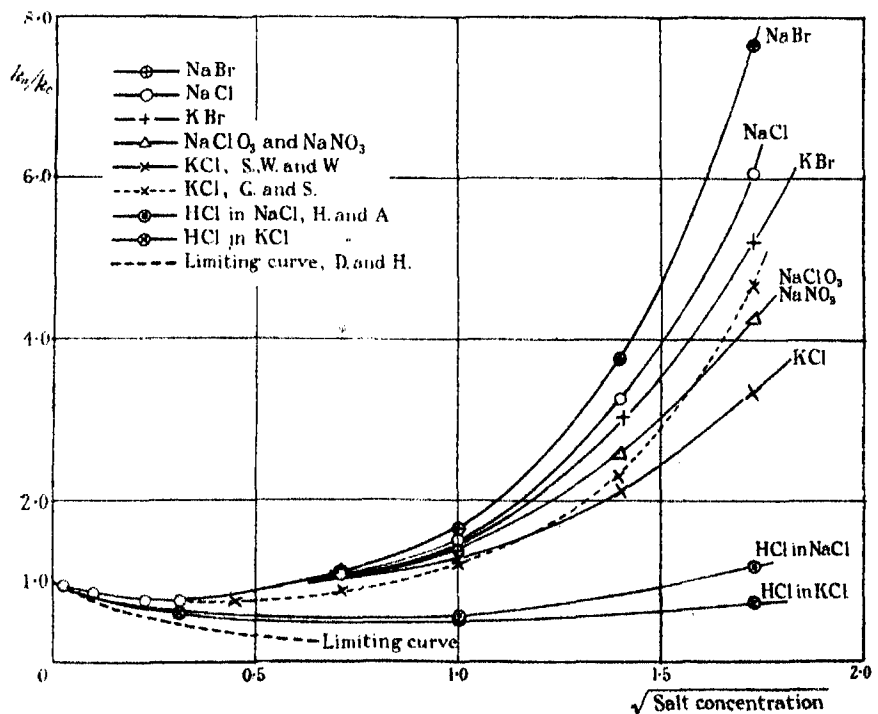
$$K_a = \frac{a_H \cdot a_A}{a_{HA}} = \frac{f_H \cdot f_A}{f_{HA}} \times \frac{c_H \cdot c_A}{c_{HA}} = \frac{f_H \cdot f_A}{f_{HA}} \times K_c \quad (6)$$

are thermodynamically necessary. Here *a* stands for activity, *f* for activity coefficient, and *c* for concentration; and the molecular species under con-

sideration are represented by subscripts. K_a is a true constant at a given temperature, and K_c is the classical mass-action constant of Ostwald, based upon concentrations. The presence of neutral salts will cause alterations in the individual activity coefficients; the value of the function $f_H \cdot f_A / f_{HA}$ will therefore change, and, since K_a is a true constant, the value of K_c will be altered. The apparent dissociation constant of methyl orange, whose variation in the presence of neutral salts we have measured, is the product of the dissociation constant K_c and the constant of the tautomeric equilibrium between the coloured forms of the indicator. Neutral salts would be expected to influence both of these factors, and what is observed is the total effect. If, however, we ignore the tautomeric equilibrium and apply equation (6) to the indicator acid, we have

$$\frac{K_a}{K_c} = \frac{f_H \cdot f_A}{f_{HA}}.$$

This may be called the apparent activity coefficient function for the acid. In the figure the values of the ratio K_a/K_c are plotted against the square root of the salt concentration in moles per litre. For K_a is taken the value of K_c in



absence of salt, since under these conditions all the f -values are practically equal to unity. The dotted curve shows the corresponding results from the more recent measurements of Güntelberg and Schiödt (*loc. cit.*) upon methyl orange in presence of potassium chloride, which are in fair agreement with ours.

The bulk of the experimental evidence leads us to expect that the variation of the term f_{HA} will be small compared with those of f_H and f_A ; and consequently we should expect the function $f_H \cdot f_A / f_{HA}$ for a weak acid to vary in a similar manner to the function $f_H \cdot f_A$ for a strong acid, where the concentration of the undissociated part is zero. For comparison we have plotted on fig. 1 the results of Harned and Akerlöf* for hydrochloric acid (N/1000 and N/500) in solutions of sodium chloride and potassium chloride. These are expressed in slightly different units from ours; the salt concentrations are given in molalities instead of volume normalities, and in place of the activity coefficient f we have the coefficient γ which is defined as the ratio of activity to molality. Only in very dilute solutions does the molality tend to become equal to the normality, and $\gamma = f$; but the differences are always unimportant so long as we are only concerned with the relative positions and shapes of the curves. For hydrochloric acid, therefore, we have plotted the values of $\gamma^2 = \gamma_H \cdot \gamma_{Cl}$ against the square root of the salt molality.

On the same figure is also plotted the theoretical limiting curve for very dilute solutions calculated from the equation

$$\log f = -0.354\sqrt{2c},$$

which is derivable from the Debye-Hückel theory.† This equation refers to a uni-univalent strong electrolyte in presence of a concentration c of a uni-univalent neutral salt; and $f = f_+ \cdot f_-$, where the subscripts refer to the positive and negative ions.

It will be seen from the figure that the methyl orange curves, like those for hydrochloric acid, appear to approach the theoretical in very dilute salt solutions. At any given salt concentration, however, the deviation is much more marked for the indicator than for the strong acid. The two sets of curves are alike in having a minimum, but this is at a much smaller concentration (N/20 — N/10) for the indicator, which is also very much more affected at high salt concentrations. The differences in type between the curves for hydrochloric acid and for methyl orange are presumably due to the presence

* 'Phys. Z.,' vol. 27, p. 420 (1926).

† 'Phys. Z.,' vol. 24, p. 185 (1923).

in the latter of the tautomeric equilibrium. The measurements do not permit of a separation of the salt effects upon the tautomeric and the ionic equilibria.

An important point is the order of effectiveness of the salts. We find $\text{NaBr} > \text{NaCl} > \text{KBr} > \text{KCl}$, as reckoned by the magnitude of the effect on the apparent ionisation of the acid of methyl orange, an order which is identical with that of the effect on the activity coefficient of a strong acid. This is in accordance with Hückel's theory of concentrated solutions, which states that all activity coefficients of electrolytes at a given concentration are greater in the solution possessing the higher electrical field strength. The measurements of Harned* have, however, shown that, as measured by the effect on the activity coefficients of hydroxides or on the ionic activity coefficient product of water, the salt order is reversed. This is at variance with Hückel's theory, and is explained by Harned and Akerlöf (*loc. cit.*) as due to an alteration of the free energy of the hydroxyl ion owing to a change in its electrostatic moment by the electrical field of the solution. The occurrence of this change is supposed to be connected with the unsymmetrical nature of the hydroxyl ion, which makes it deformable by the field. Measurements of the effect of salts on the velocity of hydrolysis of ethyl formate, as interpreted by Harned,† show that the salt order for formic acid is also the reverse of that for hydrochloric acid; and this again is supposed to be due to the unsymmetrical nature of the formate ion. If these considerations are correct, we should expect the salt order for methyl orange to be the same as that for hydroxides, water and formic acid; for the anion of the aci-form of the indicator must be highly unsymmetrical. Our experiments show, on the contrary, that the order for methyl orange is the same as for hydrochloric acid. It is possible however that the argument is complicated by the presence of the tautomeric indicator change, for which the nature of the salt effect cannot be foreseen.

In the experiments on methyl orange buffered with ammonia-acetic acid (Tables V and VI), the effect of the salt on the indicator is completely eliminated by using in the calculation at each salt concentration the proper value of K from Tables III and IV. This leaves us with the effect of the salts on the ionisation of the buffer solution, which is made up of the sum of the partial effects upon the acetic acid and the ammonia respectively. It is not possible to separate these partial effects; but the free hydrogen ion concentrations tabulated give a measure of the total alteration in the acidity of the buffer

* For references and a review of results, see Harned, 'Trans. Faraday Soc.,' vol. 23, p. 462 (1927).

† 'J. Amer. Chem. Soc.,' vol. 49, p. 1 (1927).

It will be seen that at small concentrations the salts cause an increase of dissociation of the buffer, and after passing through a maximum at roughly $N/2$ the degree of dissociation tends, at a salt concentration of $3N$ to $4N$, to become equal to that in a salt-free solution. The general trend of the combined salt effects on the acetic acid and the ammonia is very similar to that shown by those curves in the figure, which give the variation of the activity coefficient of the single strong electrolyte hydrochloric acid. The position of the maximum for the buffer is roughly the same ($N/2$) as that of the minimum for hydrochloric acid. When we consider the order of efficiency of the salts with the buffer, we find slight irregularities at different concentrations, which are probably due to experimental errors; but in the main the order seems to be $\text{NaBr} > \text{NaCl} > \text{KBr} > \text{KCl}$, as with methyl orange.

We wish to express our thanks to Prof. F. A. Lindemann and Dr. G. M. B. Dobson for their advice, and to Imperial Chemical Industries for a grant towards the cost of this research.

On a Symmetrical Analysis of Conical Order and its Relation to Time-Space Theory.

By ALFRED A. ROBB, Sc.D., F.R.S.

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In a paper "On the Connexion of a Certain Identity with the Extension of Conical Order to n Dimensions," which appeared in the 'Proceedings of the Cambridge Philosophical Society for July, 1928, I remarked that it was "interesting to note that Conical Order, although it might be used to construct geometries of n dimensions, will give $n - 1$ of these dimensions of one character and only one of the other." This is illustrated in Time-Space Theory where the square of the distance between two Time-Space points (x_1, y_1, z_1, t_1) , (x_2, y_2, z_2, t_2) is

$$(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2 - (t_1 - t_2)^2$$

if they lie in what I have called a separation line; while, if they lie in what I have called an inertia line, the square of the distance between is

$$(t_1 - t_2)^2 - (x_1 - x_2)^2 - (y_1 - y_2)^2 - (z_1 - z_2)^2.$$

If the Time-Space points lie in an optical line this expression is zero. It is, however, misleading in this case to say that the distance is zero.

Now those who study n dimensional geometry from the analytical standpoint like to start out from an expression for the square of the distance between two points which is symmetrical in the variables, and they are apt to feel a shudder of aesthetic horror at the fact that in Time-Space Theory one of the squares should have a different sign from the rest.

On the other hand, the fact that the ideas of congruence can be built up from purely ordinal considerations for Time-Space geometry, seems to indicate a special importance for the case where one square is of a different sign from the remaining ones.

The object of the present communication is to reconcile these two points of view.

Now, as it is well known, in ordinary three-dimensional geometry the equation

$$xy + yz + zx = 0$$

represents a quadric cone and this equation is symmetrical with respect to the three variables x, y and z . If, however, by means of real linear substitutions, we reduce it to the form of a sum of squares, one square will be of a different sign from the other two.

It seemed possible that a similar result might hold for any number of variables, and investigation showed this to be the case.

Thus with four variables X_1, X_2, X_3, X_4 , if we put

$$\begin{aligned}(X_1 + X_2 - X_3 - X_4)/\sqrt{6} &= x \\(X_1 - X_2 + X_3 - X_4)/\sqrt{6} &= y \\(X_1 - X_2 - X_3 + X_4)/\sqrt{6} &= z \\ \sqrt{3}(X_1 + X_2 + X_3 + X_4)/\sqrt{6} &= t\end{aligned}$$

we can easily verify that

$$t^2 - x^2 - y^2 - z^2 = \frac{1}{3} \{X_1X_2 + X_2X_3 + X_3X_1 + X_1X_4 + X_2X_4 + X_3X_4\}$$

The transformation has been made of such a form as to introduce a coefficient

‡ for a reason which will hereafter appear. Solving for X_1, X_2, X_3, X_4 , in terms of x, y, z, t , we get

$$\frac{\sqrt{6}}{4} \left(\frac{t}{\sqrt{3}} + x + y + z \right) = X_1,$$

$$\frac{\sqrt{6}}{4} \left(\frac{t}{\sqrt{3}} + x - y - z \right) = X_2,$$

$$\frac{\sqrt{6}}{4} \left(\frac{t}{\sqrt{3}} - x + y - z \right) = X_3,$$

$$\frac{\sqrt{6}}{4} \left(\frac{t}{\sqrt{3}} - x - y + z \right) = X_4.$$

Now, as is well known, a quadratic form in n variables can be reduced by linear substitutions to a sum of squares in an infinite number of different ways, but, provided that the substitutions are real and the number of squares is the least possible, the number affected with a particular sign is invariant.

We shall, therefore, select a particular class of real linear substitutions in order to prove that for n variables (where $n > 2$) the expression

$$\frac{2(n-2)}{n-1} \sum_{p \neq q}^{1,n} x_p x_q$$

may always be put in the form of one positive and $n-1$ negative squares. It will then follow conversely that a sum of one positive and $n-1$ negative squares may always, by means of real linear substitutions, be expressed in the above symmetrical form.

In order to show this we shall first prove that

$$\begin{aligned} & \left\{ \frac{x_1 - x_2}{\sqrt{2}} \right\}^2 + \left\{ \frac{x_1 + x_2 - 2x_3}{\sqrt{6}} \right\}^2 + \left\{ \frac{x_1 + x_2 + x_3 - 3x_4}{\sqrt{12}} \right\}^2 + \dots \\ & + \left\{ \frac{\sum_{r=1}^{(n-1)} x_r - (n-1)x_n}{\sqrt{n(n-1)}} \right\}^2 \equiv \frac{(n-1) \sum_{r=1}^n x_r^2 - 2 \sum_{p \neq q}^{1,n} x_p x_q}{n} \end{aligned}$$

where $\sum_{p \neq q}^{1,n} x_p x_q$ signifies that the summation is to be taken only for the case of p different from q .

We shall first show that if the result holds for any value of n it must hold also for $(n+1)$.

To each side of this add

$$\left\{ \frac{\sum_{r=1}^n x_r - nx_{n+1}}{\sqrt{(n+1)n}} \right\}^2$$

and the right hand side becomes

$$\frac{\sum_1^n x_r^2 + 2 \sum_1^{1,n} x_p x_q + n^2 x_{n+1}^2 - 2n x_{n+1} \sum_1^n x_r + n^2 \sum_1^n x_r^2 - 2(n+1) \sum_1^{1,n} x_p x_q}{(n+1)n}$$

$$\equiv \frac{n^2 \sum_1^{(n+1)} x_r^2 - 2n \sum_1^{1,n} x_p x_q - 2n x_{n+1} \sum_1^n x_r}{(n+1)n} \equiv \frac{n \sum_1^{(n+1)} x_r^2 - 2 \sum_1^{1,(n+1)} x_p x_q}{n+1}.$$

Thus if the result holds for any value of n it holds also for $(n+1)$. But the result clearly holds for $n=2$ and so it holds for $n=3, 4, 5, \dots$, and therefore holds in all cases.

But

$$\left\{ \sum_1^n x_r \right\}^2 \equiv \sum_1^n x_r^2 + 2 \sum_1^{1,n} x_p x_q,$$

and so

$$\left\{ \sum_1^n x_r \right\}^2 - \frac{n}{n-1} \left[\left(\frac{x_1 - x_2}{\sqrt{2}} \right)^2 + \left(\frac{x_1 + x_2 - 2x_3}{\sqrt{6}} \right)^2 + \dots \right. \\ \left. + \left\{ \frac{\sum_1^{(n-1)} x_r - (n-1)x_n}{\sqrt{n(n-1)}} \right\}^2 \right] \equiv \frac{2n}{n-1} \sum_1^{1,n} x_p x_q.$$

It is convenient to have a coefficient $2(n-2)/(n-1)$ on the right hand side (a step which is obviously only possible when $n > 2$) and so we multiply this identity by $(n-2)/n$ and get finally

$$\left\{ \sqrt{\frac{n-2}{n}} \sum_1^n x_r \right\}^2 - \frac{n-2}{n-1} \left[\left(\frac{x_1 - x_2}{\sqrt{2}} \right)^2 + \left(\frac{x_1 + x_2 - 2x_3}{\sqrt{6}} \right)^2 + \dots \right. \\ \left. + \left\{ \frac{\sum_1^{(n-1)} x_r - (n-1)x_n}{\sqrt{n(n-1)}} \right\}^2 \right] \equiv \frac{2(n-2)}{n-1} \sum_1^{1,n} x_p x_q.$$

If we write

$$\sqrt{\frac{n-2}{n}} \sum_1^n x_r = y, \quad \sqrt{\frac{n-2}{n-1}} \frac{x_1 - x_2}{\sqrt{2}} = y_1, \\ \sqrt{\frac{n-2}{n-1}} \frac{x_1 + x_2 - 2x_3}{\sqrt{6}} = y_2, \quad \text{etc.}$$

We may solve for $x_1, x_2, \dots, x_n$ in terms of them and so we can always express $y^2 - y_1^2 - y_2^2 - \dots - y_{(n-1)}^2$ in the symmetrical form $\frac{2(n-2)}{n-1} \sum_1^{1,n} x_p x_q$.

If O be the origin and P' and P'' be two other points whose co-ordinates are $(x_1', x_2', \dots x_n')$ and $(x_1'', x_2'', \dots x_n'')$ respectively, we have

$$OP'^2 = -2K \sum x_p' x_q' = b^2$$

$$OP''^2 = -2K \sum x_p'' x_q'' = c^2 \quad \text{say}$$

$$P'P''^2 = -2K \sum (x_p' - x_p'')(x_q' - x_q'') = a^2 \quad \text{say.}$$

Thus making use of the formula

$$\cos A = \frac{b^2 + c^2 - a^2}{2bc}$$

we get

$$\cos A = -\sum (x_p' x_q'' + x_p'' x_q') / 2\sqrt{\sum x_p' x_q' \cdot \sum x_p'' x_q''}.$$

The condition that OP' and OP'' may be normal is that

$$\sum (x_p' x_q'' + x_p'' x_q') = 0.$$

If P' and P'' lie respectively in the lines

$$x_1/b_1 = x_2/b_2 = \dots = x_n/b_n \quad \text{and} \quad x_1/c_1 = x_2/c_2 = \dots = x_n/c_n$$

we see that the angle between these lines will be given by

$$\cos A = -\sum (b_p c_q + b_q c_p) / 2\sqrt{\sum b_p b_q \cdot \sum c_p c_q}$$

while the condition of normality will be

$$\sum (b_p c_q + b_q c_p) = 0.$$

If we take the b 's as constants while the c 's vary, we get the $(n-1)$ fold

$$\sum (b_p x_q + b_q x_p) = 0$$

as the equation of the $(n-1)$ fold through the origin normal to the line

$$x_1/b_1 = x_2/b_2 = \dots = x_n/b_n.$$

Now let $\sum b_p = g$ and the equation of the $(n-1)$ fold may be expressed in the form

$$(g - b_1)x_1 + (g - b_2)x_2 + \dots + (g - b_n)x_n = 0.$$

If this be written

$$a_1x_1 + a_2x_2 + \dots + a_nx_n = 0$$

while

$$\sum a_p = f$$

we have

$$(n-1)g = f \quad \text{or} \quad g = f/(n-1)$$

so that

$$b_p = f/(n-1) - a_p.$$

Accordingly the equations of the line through the origin normal to the $(n-1)$ fold

$$a_1x_1 + a_2x_2 + \dots a_nx_n = 0$$

will be

$$\frac{x_1}{f/(n-1) - a_1} = \frac{x_2}{f/(n-1) - a_2} = \dots = \frac{x_n}{f/(n-1) - a_n}.$$

In particular, if the $(n-1)$ fold be

$$x_h = 0$$

it will be convenient to write it in the form $(n-1)x_h = 0$ and the equations of the line through the origin normal to it will be

$$x_1/1 = x_2/1 = \dots = x_h/(2-n) = \dots = x_n/1$$

where all the denominators are unity except that corresponding to x_h .

Now consider any two threefolds of this type, say, $x_1 = 0$ and $x_2 = 0$. The equations of the normals through the origin will be

$$x_1/(2-n) = x_2/1 = x_3/1 = \dots = x_n/1$$

and

$$x_1/1 = x_2/(2-n) = x_3/1 = \dots = x_n/1$$

respectively.

Now substituting these denominators in the general formula

$$\cos A = -\Sigma(b_p c_q + b_q c_p)/2\sqrt{\Sigma b_p b_q \cdot \Sigma c_p c_q}.$$

We can easily see that the numerator of this expression becomes $-(n-1)$ while the denominator becomes $(n-1)(n-2)$, so that we get

$$\cos A = -1/(n-2).$$

It follows, however, from symmetry that the normals to any two of the $(n-1)$ folds

$$x_1 = 0, \quad x_2 = 0, \quad x_3 = 0, \quad \dots \quad x_n = 0$$

will make this same angle with one another and the angle will in all cases be real.

In particular when $n = 4$ as in Time-Space theory, we have

$$\cos A = -\frac{1}{2}$$

so that the angle $A = \frac{2}{3}\pi$. We thus have what, at first sight appears very extraordinary, namely four lines meeting in one point and any pair of them making an angle equal to $\frac{2}{3}\pi$.

This could not, of course, occur in ordinary Euclidean geometry, since any three such lines would there have to lie in one plane.

In Time-Space theory however, although any two of the lines will lie in what I have called a separation plane, yet any three of them do not lie in a plane but in what I have called an optical threefold.

From the geometry of this type of threefold it is easy to see how this is possible.

We shall next show that for any value of n the angle between the normals to any two of the $(n - 1)$ folds

$$x_1 = 0, \quad x_2 = 0, \quad x_3 = 0 \dots x_n = 0$$

is equal to the angle between any two of the $n - 1$ lines meeting in a point in Euclidean space of $n - 2$ dimensions which are all equally inclined to one another.

In Salmon's "Analytic Geometry of Three Dimensions," article 56, it is shown that the relation between the six arcs joining four points on the surface of a sphere is :

$$\begin{vmatrix} 1 & \cos ab, & \cos ac, & \cos ad \\ \cos ba, & 1 & \cos bc, & \cos bd \\ \cos ca, & \cos cb, & 1 & \cos cd \\ \cos da, & \cos db, & \cos dc, & 1 \end{vmatrix} = 0.$$

If the angles are all equal and if the cos of any of them be z then this equation becomes :

$$\begin{vmatrix} 1, & z, & z, & z \\ z, & 1, & z, & z \\ z, & z, & 1, & z \\ z, & z, & z, & 1 \end{vmatrix} = 0.$$

By a similar method we obtain for the case of Euclidean space of m dimensions a determinant of order $m + 1$ equated to zero. That is

$$D \equiv \begin{vmatrix} 1, & z, & z, & z, & . & . & . \\ z, & 1, & z, & z, & . & . & . \\ z, & z, & 1, & z, & . & . & . \\ z, & z, & z, & 1, & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \end{vmatrix} = 0.$$

In order to evaluate this determinant we observe in the first place that if we put $z = 0$ then D becomes unity. Next adding all the remaining rows to the first row and taking the factor $(1 + mz)$ outside the determinant, we get

$$D \equiv (1 + mz) \begin{vmatrix} 1, & 1, & 1, & 1, & . & . & . \\ z, & 1, & z, & z, & . & . & . \\ z, & z, & 1, & z, & . & . & . \\ z, & z, & z, & 1, & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \end{vmatrix}$$

Next subtracting the first row of this determinant from each of the remaining rows and taking the factor $(z - 1)^m$ outside we get

$$D \equiv (1 + mz)(z - 1)^m \begin{vmatrix} 1, & 1, & 1, & 1, & . & . & . \\ 1, & 0, & 1, & 1, & . & . & . \\ 1, & 1, & 0, & 1, & . & . & . \\ 1, & 1, & 1, & 0, & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \\ . & . & . & . & . & . & . \end{vmatrix}$$

Thus putting $z = 0$, and remembering that in this case D becomes unity, we get finally

$$D \equiv (1 + mz)(1 - z)^m$$

and the equation to determine z becomes

$$(1 + mz)(1 - z)^m = 0.$$

But the repeated root $z = 1$, obviously refers to the case where the lines all coincide; so that in the case where they are distinct we must have

$$z = -1/m.$$

This will be equal to $\cos A$ provided that

$$m = n - 2,$$

which proves the theorem and agrees with what we have already seen to hold in the special case where $n = 4$.

We have seen that the line whose equations are

$$x_1/(2 - n) = x_2 = x_3 = \dots = x_n$$

is normal to the $(n - 1)$ fold whose equation is

$$x_1 = 0.$$

This line will also be normal to the parallel $(n - 1)$ fold whose equation is

$$x_1 = C.$$

The co-ordinates of the point of intersection with this threefold will therefore be

$$x_1 = C, \quad x_2 = x_3 = \dots = x_n = C/(2 - n).$$

The square of the length of the intercept of this normal measured from the origin will accordingly be given by

$$-\frac{2(n-2)}{(n-1)} \left\{ (n-1) \frac{C^2}{2-n} + \frac{1}{2}(n-1)(n-2) \frac{C^2}{(2-n)^2} \right\} = C^2,$$

so that the length of the intercept will be C , and a similar result will hold for the other x 's.

This is the reason why we introduced the coefficient $2(n-2)/(n-1)$ into the expression for the square of a length. Accordingly the interpretation of this symmetrical system of co-ordinates is seen to be that we take n separation lines through the origin making equal angles with one another of $\cos^{-1}\{-1/(n-2)\}$ and at distances $x_1, x_2, \dots, x_n$ from the origin we take $(n-1)$ folds normal to these lines and the intersection of the latter is the point whose co-ordinates are $x_1, x_2, \dots, x_n$.

Let us now return to the case of Time-Space theory and, with the usual meanings of x, y, z, t , let us introduce the variables X_1, X_2, X_3, X_4 , as previously defined.

If then

$$\frac{1}{2}\{X_1'X_2' + X_2'X_3' + X_3'X_1' + X_1'X_4' + X_2'X_4' + X_3'X_4'\}$$

be negative and equal to $-r^2$, the line joining the origin to the Time-Space point whose co-ordinates are x', y', z', t' , or X_1', X_2', X_3', X_4' is a separation line and the distance from the origin to it will be r .

If the expression be positive and equal to $\bar{r}^2$ then the line will be an inertia line and the distance will be $\bar{r}$.

If the expression be zero the line will be an optical line.

It will be observed that if three of the four co-ordinates X_1', X_2', X_3', X_4' , be zero the line will be an optical line, but, since the remaining co-ordinate may have any value, such different values may be taken as proportional to the distances measured along the optical line from the origin to the corresponding Time-Space points.

It is to be noted, however, that lengths cannot be compared along optical lines which are oblique to one another, but only along those which are co-directional.

In the author's 'Theory of Time and Space,' p. 362, the criterion that an element (x_1, y_1, z_1, t_1) should be *after* or *before* the origin is given, and, with suitable selection of the positive direction of t , is as follows:—

The element (x_1, y_1, z_1, t_1) is *after* the origin provided that

$$\begin{cases} (1) x_1^2 + y_1^2 + z_1^2 - t_1^2 \text{ is zero or negative, and} \\ (2) t_1 \text{ is positive;} \end{cases}$$

and it is *before* the origin provided that

$$\begin{cases} (1) x_1^2 + y_1^2 + z_1^2 - t_1^2 \text{ is zero or negative, and} \\ (2) t_1 \text{ is negative.} \end{cases}$$

If we use the symmetrical system of co-ordinates (X_1, X_2, X_3, X_4) given on p. 550 the conditions that (X_1', X_2', X_3', X_4') should be *after* the origin obviously become

$$\begin{cases} (1) \Sigma X_1' X_2' \text{ is zero or positive, and} \\ (2) \Sigma X_1' \text{ is positive;} \end{cases}$$

while the conditions that (X_1', X_2', X_3', X_4') should be *before* the origin become

$$\begin{cases} (1) \Sigma X_1' X_2' \text{ is zero or positive, and} \\ (2) \Sigma X_1' \text{ is negative.} \end{cases}$$

Now these conditions have been obtained from the corresponding conditions for (x, y, z, t) co-ordinates and these involved a suitable selection of the positive direction of t . If then we pass from one such symmetrical system of co-ordinates to another it is very important that the criteria of the *before* and *after* relations should not inadvertently be interchanged.

We shall accordingly investigate this point in connexion with the transformation of the symmetrical form

$$f(x_1, x_2, x_3, x_4) = x_1x_2 + x_2x_3 + x_3x_1 + x_1x_4 + x_2x_4 + x_3x_4$$

into itself by means of linear substitution.

The problem of the transformation of a quadratic form into itself was considered by Hermite in a paper in the 'Cambridge and Dublin Mathematical Journal,' vol. 9, pp. 63-67 (1854).

The method which he used may be employed in this case, giving a transformation involving six arbitrary constants. This is what one would expect in a complete solution, but nevertheless, there are certain other solutions which are not, strictly speaking, included in the formulæ obtained by Hermite's method, although easily derived from them by limiting processes.

In particular there is one class of solutions which is of special importance in our problem although not included in Hermite's formulæ.

Thus if

$$f(X_1, X_2, X_3, X_4) = f(x_1, x_2, x_3, x_4),$$

where X_1, X_2, X_3, X_4 are linear homogeneous functions of x_1, x_2, x_3, x_4 , obtained by this method, then $-X_1, -X_2, -X_3, -X_4$, will also obviously be a solution.

Hermite supposes that the variables X_r and x_r are expressed in terms of auxiliary variable ξ_r such that

$$X_r + x_r = 2\xi_r,$$

and it will be observed that this supposition excludes the cases where $X_r = -x_r$, since this would make the corresponding ξ_r 's, all zero. We shall, however, proceed to apply Hermite's method and consider these excluded cases afterwards.

We have

$$X_r + x_r = 2\xi_r.$$

Then

$$f(X_1, X_2, X_3, X_4) = f(2\xi_1 - x_1, 2\xi_2 - x_2, 2\xi_3 - x_3, 2\xi_4 - x_4).$$

Thus

$$f(X_1, X_2, X_3, X_4) = 4f(\xi_1, \xi_2, \xi_3, \xi_4) - 2 \left\{ x_1 \frac{\partial f}{\partial \xi_1} + x_2 \frac{\partial f}{\partial \xi_2} + x_3 \frac{\partial f}{\partial \xi_3} + x_4 \frac{\partial f}{\partial \xi_4} \right\} + f(x_1, x_2, x_3, x_4).$$

Then, since

$$f(X_1, X_2, X_3, X_4) = f(x_1, x_2, x_3, x_4),$$

this equation reduces to

$$x_1 \frac{\partial f}{\partial \xi_1} + x_2 \frac{\partial f}{\partial \xi_2} + x_3 \frac{\partial f}{\partial \xi_3} + x_4 \frac{\partial f}{\partial \xi_4} = 2f(\xi_1, \xi_2, \xi_3, \xi_4),$$

and it is easily verified that if we put

$$x_r = \xi_r + \sum_s \lambda_{rs} \frac{\partial f}{\partial \xi_s},$$

where the λ 's are any constants such that

$$\lambda_{rs} = -\lambda_{sr},$$

then the above equations will be satisfied. In our case these expressions for the x 's become :

$$\begin{aligned} x_1 &= \xi_1 + \lambda_{12}(\xi_3 + \xi_4 + \xi_1) + \lambda_{13}(\xi_4 + \xi_1 + \xi_2) + \lambda_{14}(\xi_1 + \xi_2 + \xi_3), \\ x_2 &= \xi_2 + \lambda_{21}(\xi_3 + \xi_3 + \xi_4) + \lambda_{23}(\xi_4 + \xi_1 + \xi_2) + \lambda_{24}(\xi_1 + \xi_2 + \xi_3), \\ x_3 &= \xi_3 + \lambda_{31}(\xi_2 + \xi_3 + \xi_4) + \lambda_{32}(\xi_3 + \xi_4 + \xi_1) + \lambda_{34}(\xi_1 + \xi_2 + \xi_3), \\ x_4 &= \xi_4 + \lambda_{41}(\xi_2 + \xi_3 + \xi_4) + \lambda_{42}(\xi_3 + \xi_4 + \xi_1) + \lambda_{43}(\xi_4 + \xi_1 + \xi_2). \end{aligned}$$

These may be written in the form

$$\begin{aligned} 1 + \lambda_{12} + \lambda_{13} + \lambda_{14}) \xi_1 + (\lambda_{13} + \lambda_{14}) \xi_2 + (\lambda_{12} + \lambda_{14}) \xi_3 + (\lambda_{12} + \lambda_{13}) \xi_4 &= x_1, \\ (\lambda_{23} + \lambda_{24}) \xi_1 + (1 + \lambda_{21} + \lambda_{23} + \lambda_{24}) \xi_2 + (\lambda_{21} + \lambda_{24}) \xi_3 + (\lambda_{21} + \lambda_{23}) \xi_4 &= x_2, \\ (\lambda_{32} + \lambda_{34}) \xi_1 + (\lambda_{31} + \lambda_{34}) \xi_2 + (1 + \lambda_{31} + \lambda_{32} + \lambda_{34}) \xi_3 + (\lambda_{31} + \lambda_{32}) \xi_4 &= x_3, \\ (\lambda_{43} + \lambda_{42}) \xi_1 + (\lambda_{41} + \lambda_{43}) \xi_2 + (\lambda_{41} + \lambda_{42}) \xi_3 + (1 + \lambda_{41} + \lambda_{42} + \lambda_{43}) \xi_4 &= x_4. \end{aligned}$$

and these equations may be solved for $\xi_1, \xi_2, \xi_3, \xi_4$ in terms of x_1, x_2, x_3, x_4 .

Let the determinant

$$\begin{vmatrix} (1 + \lambda_{12} + \lambda_{13} + \lambda_{14}), & (\lambda_{13} + \lambda_{14}), & (\lambda_{12} + \lambda_{14}), & (\lambda_{12} + \lambda_{13}) \\ (\lambda_{23} + \lambda_{24}), & (1 + \lambda_{21} + \lambda_{23} + \lambda_{24}), & (\lambda_{21} + \lambda_{24}), & (\lambda_{21} + \lambda_{23}) \\ (\lambda_{32} + \lambda_{34}), & (\lambda_{31} + \lambda_{34}), & (1 + \lambda_{31} + \lambda_{32} + \lambda_{34}), & (\lambda_{31} + \lambda_{32}) \\ (\lambda_{43} + \lambda_{42}), & (\lambda_{41} + \lambda_{43}), & (\lambda_{41} + \lambda_{42}), & (1 + \lambda_{41} + \lambda_{42} + \lambda_{43}) \end{vmatrix}$$

be denoted by Δ . Then

$$X_1 = 2\xi_1 - x_1$$

or

$$X_1 = 2 \frac{\begin{vmatrix} x_1, & (\lambda_{13} + \lambda_{14}), & (\lambda_{12} + \lambda_{14}), & (\lambda_{12} + \lambda_{13}) \\ x_2, & (1 + \lambda_{21} + \lambda_{23} + \lambda_{24}), & (\lambda_{21} + \lambda_{24}), & (\lambda_{21} + \lambda_{23}) \\ x_3, & (\lambda_{31} + \lambda_{34}), & (1 + \lambda_{31} + \lambda_{32} + \lambda_{34}), & (\lambda_{31} + \lambda_{32}) \\ x_4, & (\lambda_{41} + \lambda_{43}), & (\lambda_{41} + \lambda_{42}), & (1 + \lambda_{41} + \lambda_{42} + \lambda_{43}) \end{vmatrix}}{\Delta} - x_1$$

with corresponding expressions for X_2, X_3 and X_4 . This is the result of applying Hermite's method to the quadratic form :

$$x_1x_2 + x_2x_3 + x_3x_1 + x_1x_4 + x_2x_4 + x_3x_4,$$

and we shall refer to it as *Hermite's Transformation*. As we have seen, however, these expressions with their signs all reversed must also give a transformation

of the quadratic form into itself, and, as it is most important for our purpose to distinguish these two cases, we shall refer to the latter as the *Reversed Transformation*.

We shall now proceed to evaluate the determinant Δ .

In order to do so we shall make use of the following general theorem in determinants :—

If in any determinant of the n th order each row (or column) be replaced by the sum of the remaining rows (or columns) then the resulting determinant is equal to $(n-1)(-1)^{n-1}$ times the original determinant.*

Applying this to Δ and remembering that $\lambda_{pq} = -\lambda_{qp}$ we get

$$3\Delta = \begin{vmatrix} 0 & (1+\lambda_{21}+\lambda_{23}+\lambda_{24} & (1+\lambda_{31}+\lambda_{32}+\lambda_{34} & (1+\lambda_{41}+\lambda_{42}+\lambda_{43} \\ & +\lambda_{31}+\lambda_{41}), & +\lambda_{41}+\lambda_{21}), & +\lambda_{21}+\lambda_{31}) \\ (1+\lambda_{12}+\lambda_{13}+\lambda_{14} & 0 & (1+\lambda_{31}+\lambda_{32}+\lambda_{34} & (1+\lambda_{41}+\lambda_{42}+\lambda_{43} \\ +\lambda_{22}+\lambda_{42}), & & +\lambda_{12}+\lambda_{42}), & \lambda_{22}+\lambda_{12}) \\ (1+\lambda_{12}+\lambda_{13}+\lambda_{14} & (1+\lambda_{21}+\lambda_{23}+\lambda_{24} & 0 & (1+\lambda_{41}+\lambda_{42}+\lambda_{43} \\ +\lambda_{43}+\lambda_{23}), & +\lambda_{43}+\lambda_{13}), & & +\lambda_{13}+\lambda_{23}) \\ (1+\lambda_{12}+\lambda_{13}+\lambda_{14} & (1+\lambda_{21}+\lambda_{23}+\lambda_{24} & (1+\lambda_{31}+\lambda_{32}+\lambda_{34} & 0 \\ +\lambda_{24}+\lambda_{34}), & +\lambda_{14}+\lambda_{34}), & +\lambda_{24}+\lambda_{14}), & \end{vmatrix}$$

This determinant may be raised to one of the fifth order by bordering it with a row of five 1's and making the first column a 1 and four 0's. If then we

* This result is probably well known, but in any case, it is easily proved.

Writing the first row of a determinant Δ of the n th order instead of the whole determinant thus :

$$\Delta = |a_{11}, a_{12}, a_{13}, \dots, a_{1n}|$$

and putting

$$s_1 = a_{11} + a_{12} + a_{13} + \dots + a_{1n}$$

we have

$$\Delta = |s_1, a_{12}, a_{13}, \dots, a_{1n}|$$

$$(-1)^{n-1} \Delta = |s_1, -a_{12}, -a_{13}, \dots, -a_{1n}|.$$

Adding the first column to each of the remaining columns we get

$$(-1)^{n-1} \Delta = |s_1, (s_1 - a_{12}), (s_1 - a_{13}), \dots, (s_1 - a_{1n})|$$

$$(n-1)(-1)^{n-1} \Delta = |(n-1)s_1, (s_1 - a_{12}), (s_1 - a_{13}), \dots, (s_1 - a_{1n})|.$$

Adding the last $n-1$ columns and subtracting from the first we get :

$$(n-1)(-1)^{n-1} \Delta = |(s_1 - a_{11}), (s_1 - a_{12}), (s_1 - a_{13}), \dots, (s_1 - a_{1n})|.$$

A similar result may be obtained interchanging rows and columns.

subtract the first row from each of the others we obtain a skew determinant of the fifth order which we may write in the form :

$$-3\Delta = \begin{vmatrix} 1, & 1 & , & 1 & , & 1 & , & 1 \\ -1, & -1 & , & (\lambda_{21} + \lambda_{23} + \lambda_{24} & + \lambda_{31} + \lambda_{41}), & (\lambda_{21} + \lambda_{32} + \lambda_{34} & + \lambda_{41} + \lambda_{21}), & (\lambda_{41} + \lambda_{42} + \lambda_{43} & + \lambda_{21} + \lambda_{31}) \\ -1, & (\lambda_{12} + \lambda_{13} + \lambda_{14} & + \lambda_{32} + \lambda_{42}), & -1 & , & (\lambda_{31} + \lambda_{32} + \lambda_{34} & + \lambda_{12} + \lambda_{42}), & (\lambda_{41} + \lambda_{42} + \lambda_{43} & + \lambda_{32} + \lambda_{12}) \\ -1, & (\lambda_{12} + \lambda_{13} + \lambda_{14} & + \lambda_{43} + \lambda_{23}), & (\lambda_{21} + \lambda_{23} + \lambda_{24} & + \lambda_{43} + \lambda_{13}), & -1 & , & (\lambda_{41} + \lambda_{42} + \lambda_{43} & + \lambda_{13} + \lambda_{23}) \\ -1, & (\lambda_{12} + \lambda_{13} + \lambda_{14} & + \lambda_{24} + \lambda_{34}), & (\lambda_{21} + \lambda_{23} + \lambda_{24} & + \lambda_{14} + \lambda_{34}), & (\lambda_{31} + \lambda_{32} + \lambda_{34} & + \lambda_{24} + \lambda_{14}), & -1 \end{vmatrix}.$$

Expanding this by the usual method for expanding skew determinants we get :—

$$\begin{aligned} -3\Delta &= 1 + (\lambda_{21} + \lambda_{23} + \lambda_{24} + \lambda_{31} + \lambda_{41})^2 + (\lambda_{31} + \lambda_{32} + \lambda_{34} + \lambda_{41} + \lambda_{21})^2 \\ &+ (\lambda_{41} + \lambda_{42} + \lambda_{43} + \lambda_{21} + \lambda_{31})^2 + (\lambda_{31} + \lambda_{32} + \lambda_{34} + \lambda_{12} + \lambda_{42})^2 \\ &+ (\lambda_{41} + \lambda_{42} + \lambda_{43} + \lambda_{32} + \lambda_{12})^2 + (\lambda_{41} + \lambda_{42} + \lambda_{43} + \lambda_{13} + \lambda_{23})^2 \\ &- 4 + 9\{\lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32}\}^2 \\ &- (\lambda_{34} + \lambda_{42} + \lambda_{23})^2 - (\lambda_{41} + \lambda_{13} + \lambda_{34})^2 \\ &- (\lambda_{12} + \lambda_{24} + \lambda_{41})^2 - (\lambda_{23} + \lambda_{31} + \lambda_{12})^2, \end{aligned}$$

or

$$\begin{aligned} -3\Delta &= -3 + 3\{\lambda_{34}^2 + \lambda_{42}^2 + \lambda_{23}^2 + \lambda_{41}^2 + \lambda_{13}^2 + \lambda_{12}^2\} \\ &+ 9\{\lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32}\}^2 \\ &+ 6\{\lambda_{41}\lambda_{42} + \lambda_{43}\lambda_{23} + \lambda_{43}\lambda_{41} + \lambda_{43}\lambda_{13} \\ &+ \lambda_{42}\lambda_{32} + \lambda_{42}\lambda_{41} + \lambda_{42}\lambda_{12} + \lambda_{23}\lambda_{13} \\ &+ \lambda_{23}\lambda_{21} + \lambda_{41}\lambda_{31} + \lambda_{41}\lambda_{21} + \lambda_{13}\lambda_{12}\}. \end{aligned}$$

It will be observed that there are no products of λ 's containing all four suffixes in the last term. Thus we get

$$\begin{aligned} \Delta &= 1 + (\lambda_{34} + \lambda_{42} + \lambda_{23})^2 + (\lambda_{41} + \lambda_{13} + \lambda_{34})^2 \\ &+ (\lambda_{12} + \lambda_{24} + \lambda_{41})^2 + (\lambda_{23} + \lambda_{31} + \lambda_{12})^2 \\ &- 3\{\lambda_{34}^2 + \lambda_{42}^2 + \lambda_{23}^2 + \lambda_{41}^2 + \lambda_{31}^2 + \lambda_{21}^2\} \\ &- 3\{\lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32}\}^2. \end{aligned}$$

Our problem is to find how the signs of the corresponding symmetrical expressions

$$x_1 + x_2 + x_3 + x_4$$

and

$$X_1 + X_2 + X_3 + X_4$$

are related for a given transformation when our quadratic form is zero or positive.

Now it will be observed that the coefficients of x_1 in X_1, X_2, X_3 and X_4 will respectively be of the forms :

$$2a/\Delta - 1, \quad 2b/\Delta, \quad 2c/\Delta, \quad 2d/\Delta$$

where a, b, c and d are the coefficients of

$$(1 + \lambda_{12} + \lambda_{13} + \lambda_{14}), \quad (\lambda_{13} + \lambda_{14}), \quad (\lambda_{12} + \lambda_{14}), \quad (\lambda_{12} + \lambda_{13})$$

respectively in the expansion of the determinant Δ .

It is thus clear that $(a + b + c + d)$ must be the determinant :

$$\begin{vmatrix} 1 & , & 1 & , & 1 & , & 1 \\ (\lambda_{23} + \lambda_{24}), & (1 + \lambda_{21} + \lambda_{23} + \lambda_{24}), & (\lambda_{21} + \lambda_{24}), & (\lambda_{21} + \lambda_{23}) \\ (\lambda_{32} + \lambda_{34}), & (\lambda_{31} + \lambda_{34}), & (1 + \lambda_{31} + \lambda_{32} + \lambda_{34}), & (\lambda_{31} + \lambda_{32}) \\ (\lambda_{43} + \lambda_{42}), & (\lambda_{41} + \lambda_{43}), & (\lambda_{41} + \lambda_{42}), & (1 + \lambda_{41} + \lambda_{42} + \lambda_{43}) \end{vmatrix}$$

which we shall denote by α ; and we shall denote by β, γ and δ the corresponding determinants obtained by replacing the second, third and fourth rows respectively of Δ by rows of units.

It will thus be seen that the coefficients of x_1, x_2, x_3, x_4 in the expression for $X_1 + X_2 + X_3 + X_4$ will be respectively :

$$\frac{2\alpha - \Delta}{\Delta}, \quad \frac{2\beta - \Delta}{\Delta}, \quad \frac{2\gamma - \Delta}{\Delta}, \quad \frac{2\delta - \Delta}{\Delta}.$$

We have next to evaluate the determinant α . Subtracting the first column from each of the others we get

$$\begin{aligned} \alpha &= \begin{vmatrix} 1 & , & 0 & , & 0 & , & 0 \\ (\lambda_{23} + \lambda_{24}), & (1 + \lambda_{21}), & (\lambda_{21} - \lambda_{23}), & (\lambda_{21} - \lambda_{24}) \\ (\lambda_{32} + \lambda_{34}), & (\lambda_{31} - \lambda_{32}), & (1 + \lambda_{31}), & (\lambda_{31} - \lambda_{34}) \\ (\lambda_{43} + \lambda_{42}), & (\lambda_{43} - \lambda_{42}), & (\lambda_{41} - \lambda_{43}), & (1 + \lambda_{41}) \end{vmatrix} \\ &= \begin{vmatrix} & (1 + \lambda_{21}), & (\lambda_{21} - \lambda_{23}), & (\lambda_{21} - \lambda_{24}) \\ & (\lambda_{31} - \lambda_{32}), & (1 + \lambda_{31}), & (\lambda_{31} - \lambda_{34}) \\ & (\lambda_{41} - \lambda_{42}), & (\lambda_{41} - \lambda_{43}), & (1 + \lambda_{41}) \end{vmatrix} \end{aligned}$$

Expanding this we find that

$$\begin{aligned}\alpha = 1 &+ (\lambda_{21} + \lambda_{31} + \lambda_{41}) + \lambda_{21}(\lambda_{32} + \lambda_{42}) + \lambda_{31}(\lambda_{43} + \lambda_{23}) \\ &+ \lambda_{41}(\lambda_{24} + \lambda_{34}) + (\lambda_{34}^2 + \lambda_{42}^2 + \lambda_{23}^2) \\ &+ (\lambda_{21}\lambda_{34} + \lambda_{31}\lambda_{42} + \lambda_{41}\lambda_{23})(\lambda_{34} + \lambda_{42} + \lambda_{23})\end{aligned}$$

and we obtain similar expressions for β , γ and δ .

We have next to show that the expressions

$$2\alpha - \Delta, \quad 2\beta - \Delta, \quad 2\gamma - \Delta, \quad 2\delta - \Delta$$

which we shall denote by A, B, C, D, respectively, are essentially positive.

We have

$$\begin{aligned}2\alpha - \Delta &= 2 + 2(\lambda_{21} + \lambda_{31} + \lambda_{41}) + 2\lambda_{21}(\lambda_{32} + \lambda_{42}) + 2\lambda_{31}(\lambda_{43} + \lambda_{23}) \\ &+ 2\lambda_{41}(\lambda_{24} + \lambda_{34}) + 2(\lambda_{34}^2 + \lambda_{42}^2 + \lambda_{23}^2) \\ &+ 2(\lambda_{21}\lambda_{34} + \lambda_{31}\lambda_{42} + \lambda_{41}\lambda_{23})(\lambda_{34} + \lambda_{42} + \lambda_{23}) \\ &- 1 + 3(\lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32})^2 \\ &+ \lambda_{34}^2 + \lambda_{42}^2 + \lambda_{23}^2 + \lambda_{21}^2 + \lambda_{31}^2 + \lambda_{41}^2 \\ &- 2(\lambda_{34}\lambda_{42} + \lambda_{42}\lambda_{23} + \lambda_{23}\lambda_{34} + \lambda_{41}\lambda_{13} + \lambda_{13}\lambda_{34} + \lambda_{34}\lambda_{41} \\ &+ \lambda_{12}\lambda_{24} + \lambda_{24}\lambda_{41} + \lambda_{41}\lambda_{12} + \lambda_{23}\lambda_{31} + \lambda_{31}\lambda_{12} + \lambda_{12}\lambda_{23}) \\ &= (1 + \lambda_{21} + \lambda_{31} + \lambda_{41})^2 + 3\lambda_{34}^2 + 3\lambda_{42}^2 + 3\lambda_{23}^2 \\ &+ 3(\lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32})^2 \\ &+ 2(\lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32})(\lambda_{34} + \lambda_{42} + \lambda_{23}) \\ &- 2(\lambda_{34}\lambda_{42} + \lambda_{42}\lambda_{23} + \lambda_{23}\lambda_{34}).\end{aligned}$$

But we have the identity

$$\begin{aligned}3(w^2 + x^2 + y^2 + z^2) + 2w(x + y + z) - 2(yz + zx + xy) \\ \equiv (w + y + z - x)^2 + (w + z + x - y)^2 + (w + x + y - z)^2.\end{aligned}$$

Thus writing

$$x = \lambda_{34} = -\lambda_{43}, \quad y = \lambda_{42} = -\lambda_{24}, \quad z = \lambda_{23} = -\lambda_{32},$$

$$w = (\lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32})$$

we get:

$$\begin{aligned}A = 2\alpha - \Delta &= (1 + \lambda_{21} + \lambda_{31} + \lambda_{41})^2 + (w + \lambda_{42} + \lambda_{43} + \lambda_{23})^2 \\ &+ (w + \lambda_{23} + \lambda_{24} + \lambda_{34})^2 + (w + \lambda_{24} + \lambda_{32} + \lambda_{42})^2,\end{aligned}$$

which, being a sum of four squares, is essentially positive.

Similarly B, C and D are also essentially positive.

We have next to prove that

$$(\alpha + \beta + \gamma + \delta)(\alpha + \beta + \gamma + \delta - \Delta) = 3(\alpha^2 + \beta^2 + \gamma^2 + \delta^2)$$

as a preliminary to proving that

$$\Sigma AB - \Sigma A^2 = 2\Delta^2.$$

In order to do this we shall first obtain expressions for $(\alpha + \beta + \gamma + \delta)$ and $(\alpha + \beta + \gamma + \delta - \Delta)$.

Now it is easily seen that

$$\Sigma(\lambda_{21}\lambda_{34} + \lambda_{31}\lambda_{42} + \lambda_{41}\lambda_{23})(\lambda_{34} + \lambda_{42} + \lambda_{23}) = 0$$

and

$$\Sigma(\lambda_{21} + \lambda_{31} + \lambda_{41}) = 0.$$

Thus reverting to the expression for α we see at once that

$$\begin{aligned} \alpha + \beta + \gamma + \delta = 4 + (\lambda_{34} + \lambda_{42} + \lambda_{23})^2 + (\lambda_{41} + \lambda_{13} + \lambda_{24})^2 \\ + (\lambda_{12} + \lambda_{24} + \lambda_{41})^2 + (\lambda_{23} + \lambda_{31} + \lambda_{12})^2. \end{aligned}$$

But now

$$\begin{aligned} 2\{\lambda_{34} + \lambda_{42} + \lambda_{23} + \lambda_{14} + \lambda_{31} + \lambda_{43} + \lambda_{12} \\ + \lambda_{24} + \lambda_{41} + \lambda_{32} + \lambda_{13} + \lambda_{21}\} = 0. \end{aligned}$$

Thus we get

$$\begin{aligned} (\alpha + \beta + \gamma + \delta) = (1 + \lambda_{34} + \lambda_{42} + \lambda_{23})^2 + (1 + \lambda_{14} + \lambda_{31} + \lambda_{43})^2 \\ + (1 + \lambda_{12} + \lambda_{24} + \lambda_{41})^2 + (1 + \lambda_{32} + \lambda_{13} + \lambda_{21})^2 \end{aligned}$$

a sum of four squares.

Again

$$\begin{aligned} (\alpha + \beta + \gamma + \delta - \Delta) = 3\{1 + (\lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32})^2 \\ + \lambda_{34}^2 + \lambda_{42}^2 + \lambda_{23}^2 + \lambda_{21}^2 + \lambda_{31}^2 + \lambda_{41}^2\}, \end{aligned}$$

which may be written in the form :

$$\begin{aligned} 3\{(1 + \lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32})^2 + (\lambda_{43} + \lambda_{21})^2 \\ + (\lambda_{24} + \lambda_{31})^2 + (\lambda_{32} + \lambda_{41})^2\}. \end{aligned}$$

Now we propose to make use of Euler's identity :

$$\begin{aligned} (a^2 + b^2 + c^2 + d^2)(a'^2 + b'^2 + c'^2 + d'^2) \\ \equiv (aa' + bb' + cc' + dd')^2 + (ab' - a'b + dc' - d'c)^2 \\ + (ac' - a'c + bd' - b'd)^2 + (ad' - a'd + cb' - c'b)^2 \end{aligned}$$

in order to form the product of the above two expressions.

Put

$$\begin{aligned} a &= (1 + \lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32}), & a' &= (1 + \lambda_{34} + \lambda_{42} + \lambda_{23}), \\ b &= (\lambda_{43} + \lambda_{21}), & b' &= (1 + \lambda_{14} + \lambda_{31} + \lambda_{42}), \\ c &= (\lambda_{24} + \lambda_{31}), & c' &= (1 + \lambda_{12} + \lambda_{24} + \lambda_{41}), \\ d &= (\lambda_{32} + \lambda_{41}), & d' &= (1 + \lambda_{32} + \lambda_{13} + \lambda_{21}). \end{aligned}$$

Then

$$\begin{aligned} aa' + bb' + cc' + dd' &= (1 + \lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32}) (1 + \lambda_{34} + \lambda_{42} + \lambda_{23}) \\ &\quad + (\lambda_{43} + \lambda_{21}) (1 + \lambda_{14} + \lambda_{31} + \lambda_{42}) \\ &\quad + (\lambda_{24} + \lambda_{31}) (1 + \lambda_{12} + \lambda_{24} + \lambda_{41}) \\ &\quad + (\lambda_{32} + \lambda_{41}) (1 + \lambda_{32} + \lambda_{13} + \lambda_{21}). \\ &= 1 + (\lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32}) \\ &\quad + (\lambda_{12}\lambda_{34} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32}) (\lambda_{34} + \lambda_{42} + \lambda_{23}) \\ &\quad + (\lambda_{21} + \lambda_{31} + \lambda_{41}) + (\lambda_{43}^2 + \lambda_{24}^2 + \lambda_{32}^2) \\ &\quad + (\lambda_{43}\lambda_{14} + \lambda_{43}\lambda_{31} + \lambda_{24}\lambda_{12} + \lambda_{24}\lambda_{41} + \lambda_{32}\lambda_{13} + \lambda_{32}\lambda_{21}) \\ &\quad + (\lambda_{21}\lambda_{14} + \lambda_{21}\lambda_{31} + \lambda_{21}\lambda_{43} + \lambda_{31}\lambda_{12} + \lambda_{31}\lambda_{24} \\ &\quad + \lambda_{31}\lambda_{41} + \lambda_{41}\lambda_{32} + \lambda_{41}\lambda_{13} + \lambda_{41}\lambda_{21}) \\ &= 1 + (\lambda_{21} + \lambda_{31} + \lambda_{41}) + (\lambda_{43}^2 + \lambda_{24}^2 + \lambda_{32}^2) + \lambda_{21}(\lambda_{32} + \lambda_{42}) \\ &\quad + \lambda_{31}(\lambda_{43} + \lambda_{23}) + \lambda_{41}(\lambda_{24} + \lambda_{34}) + (\lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32}) \\ &\quad (\lambda_{34} + \lambda_{42} + \lambda_{23}), \\ &= \alpha. \end{aligned}$$

Similarly

$$\begin{aligned} a'' - a'b + dc' - d'c &= \beta, \\ ac' - a'c + bd' - b'd &= \gamma, \\ ad' - a'd + cb' - c'b &= \delta. \end{aligned}$$

Thus

$$\begin{aligned} (\alpha + \beta + \gamma + \delta)(\alpha + \beta + \gamma + \delta - \Delta) &= 3(\alpha^2 + \beta^2 + \gamma^2 + \delta^2)^* \\ \text{or} &(\Sigma\alpha)^2 - \Delta \cdot \Sigma\alpha - 3\Sigma\alpha^2 = 0. \end{aligned}$$

* For the case of three variables the corresponding result takes the form :

$$(\alpha + \beta + \gamma)(\alpha + \beta + \gamma - \Delta) = 2(\alpha^2 + \beta^2 + \gamma^2).$$

This suggests a probable general theorem for n variables

$$(\Sigma\alpha)(\Sigma\alpha - \Delta) = (n-1)(\Sigma\alpha^2),$$

which, however, I have not yet proved.

Now

$$A = 2\alpha - \Delta, \quad B = 2\beta - \Delta, \quad C = 2\gamma - \Delta, \quad D = 2\delta - \Delta,$$

$$A^2 = 4\alpha^2 - 4\Delta\alpha + \Delta^2,$$

$$AB = 4\alpha\beta - 2\Delta(\alpha + \beta) + \Delta^2,$$

Thus

$$\Sigma A^2 = 4\Sigma\alpha^2 - 4\Delta\Sigma\alpha + 4\Delta^2,$$

and

$$\Sigma AB = 4\Sigma\alpha\beta - 6\Delta\Sigma\alpha + 6\Delta^2$$

$$= 2(\Sigma\alpha)^2 - 2\Sigma\alpha^2 - 6\Delta\Sigma\alpha + 6\Delta^2,$$

so that we get

$$\Sigma AB - \Sigma A^2 = 2\{(\Sigma\alpha)^2 - \Delta\Sigma\alpha - 3\Sigma\alpha^2\} + 2\Delta^2.$$

But we have seen that

$$(\Sigma\alpha)^2 - \Delta\Sigma\alpha - 3\Sigma\alpha^2 = 0,$$

so that we get

$$\Sigma AB - \Sigma A^2 = 2\Delta^2.$$

We see now that in the case of Hermite's transformation we have

$$X_1 + X_2 + X_3 + X_4 = (Ax_1 + Bx_2 + Cx_3 + Dx_4)/\Delta,$$

where A, B, C, and D are essentially positive and where

$$\Sigma AB - \Sigma A^2 = 2\Delta^2,$$

which is also an essentially positive quantity.

Now let us form the product

$$(Ax_1 + Bx_2 + Cx_3 + Dx_4)(x_1 + x_2 + x_3 + x_4).$$

It is

$$\begin{aligned} & Ax_1^2 + Bx_2^2 + Cx_3^2 + Dx_4^2 + (A+B)x_1x_2 + (B+C)x_2x_3 + (C+A)x_3x_1 \\ & + (A+D)x_1x_4 + (B+D)x_2x_4 + (C+D)x_3x_4. \end{aligned}$$

This may be put in the form :

$$\begin{aligned} & [Ax_1^2 + Bx_2^2 + Cx_3^2 + Dx_4^2 + (\omega - C - D)x_1x_2 + (\omega - D - A)x_2x_3 \\ & + (\omega - D - B)x_3x_1 + (\omega - B - C)x_1x_4 + (\omega - A - C)x_2x_4 + (\omega - B - A)x_3x_4] \\ & + \frac{1}{3}(A+B+C+D)(x_1x_2 + x_2x_3 + x_3x_1 + x_1x_4 + x_2x_4 + x_3x_4); \end{aligned}$$

where

$$\omega = \frac{2}{3}(A+B+C+D),$$

this value of ω being selected because it will be found hereafter to simplify our result.

We shall prove that the portion of the above expression which is enclosed in square brackets will in this case be a positive quadratic form.

Now it is known that a quadratic form

$$a_{11}x_1^2 + a_{22}x_2^2 + a_{33}x_3^2 + a_{44}x_4^2 + 2a_{12}x_1x_2 + 2a_{23}x_2x_3 + 2a_{31}x_3x_1 \\ + 2a_{14}x_1x_4 + 2a_{24}x_2x_4 + 2a_{34}x_3x_4$$

may be expressed as a sum of squares with positive coefficients provided that the roots of the discriminating determinantal equation

$$\begin{vmatrix} (a_{11} - \theta), & a_{12}, & a_{13}, & a_{14} \\ a_{21}, & (a_{22} - \theta), & a_{23}, & a_{24} \\ a_{31}, & a_{32}, & (a_{33} - \theta), & a_{34} \\ a_{41}, & a_{42}, & a_{43}, & (a_{44} - \theta) \end{vmatrix} = 0$$

(where $a_{pq} = a_{qp}$) are all positive.

Now in our case

$$a_{11} = A, \quad a_{22} = B, \quad a_{33} = C, \quad a_{44} = D, \\ a_{12} = \frac{1}{2}(\omega - C - D), \quad a_{23} = \frac{1}{2}(\omega - D - A), \quad a_{31} = \frac{1}{2}(\omega - D - B), \\ a_{14} = \frac{1}{2}(\omega - B - C), \quad a_{24} = \frac{1}{2}(\omega - A - C), \quad a_{34} = \frac{1}{2}(\omega - B - A),$$

where $\omega = \frac{2}{3}(A + B + C + D)$.

This selected value of ω gives

$$a_{11} - a_{12} - a_{13} - a_{14} = 0, \quad a_{22} - a_{23} - a_{24} - a_{21} = 0, \\ a_{33} - a_{34} - a_{31} - a_{32} = 0, \quad a_{44} - a_{41} - a_{42} - a_{43} = 0,$$

and ω is a positive fractional part of $(A + B + C + D)$, which constitute the reasons for selecting it.

Let

$$a_{pq} = a_{qp} \\ a_{11} - a_{12} - a_{13} - a_{14} = 0, \quad a_{22} - a_{23} - a_{24} - a_{21} = 0, \\ a_{33} - a_{34} - a_{31} - a_{32} = 0, \quad a_{44} - a_{41} - a_{42} - a_{43} = 0.$$

It is required to simplify the determinant :

$$G = \begin{vmatrix} (a_{11} - \theta), & a_{12}, & a_{13}, & a_{14} \\ a_{21}, & (a_{22} - \theta), & a_{23}, & a_{24} \\ a_{31}, & a_{32}, & (a_{33} - \theta), & a_{34} \\ a_{41}, & a_{42}, & a_{43}, & (a_{44} - \theta) \end{vmatrix}.$$

Subtracting the last three rows from the first row we get in virtue of the above relations among the a 's :

$$G = \begin{vmatrix} -\theta, & (\theta - 2a_{23} - 2a_{24}), & (\theta - 2a_{32} - 2a_{34}), & (\theta - 2a_{43} - 2a_{42}) \\ a_{21}, & (a_{22} - \theta), & a_{23}, & a_{24} \\ a_{31}, & a_{32}, & (a_{33} - \theta), & a_{34} \\ a_{41}, & a_{42}, & a_{43}, & (a_{44} - \theta) \end{vmatrix}.$$

Similarly subtracting the first, third and fourth columns from the second one we get :

$$G = \begin{vmatrix} -\theta, & 4a_{34}, & (\theta - 2a_{32} - 2a_{34}), & (\theta - 2a_{43} - 2a_{42}) \\ a_{21}, & -\theta, & a_{23}, & a_{24} \\ a_{31}, & (\theta - 2a_{34} - 2a_{31}), & (a_{33} - \theta), & a_{34} \\ a_{41}, & (\theta - 2a_{43} - 2a_{41}), & a_{43}, & (a_{44} - \theta) \end{vmatrix}.$$

Dividing first row and second column by 2 and bringing a factor 4 outside determinant, we get :

$$G = 4 \begin{vmatrix} -\frac{1}{2}\theta, & a_{34}, & (\frac{1}{2}\theta - a_{32} - a_{34}), & (\frac{1}{2}\theta - a_{43} - a_{42}) \\ a_{21}, & -\frac{1}{2}\theta, & a_{23}, & a_{24} \\ a_{31}, & (\frac{1}{2}\theta - a_{34} - a_{31}), & (a_{33} - \theta), & a_{34} \\ a_{41}, & (\frac{1}{2}\theta - a_{43} - a_{41}), & a_{43}, & (a_{44} - \theta) \end{vmatrix}.$$

Adding second column to the third and fourth we get :

$$G = 4 \begin{vmatrix} -\frac{1}{2}\theta, & a_{34}, & (\frac{1}{2}\theta - a_{32}), & (\frac{1}{2}\theta - a_{42}) \\ a_{21}, & -\frac{1}{2}\theta, & (a_{23} - \frac{1}{2}\theta), & (a_{24} - \frac{1}{2}\theta) \\ a_{31}, & (\frac{1}{2}\theta - a_{34} - a_{31}), & (a_{33} - a_{34} - a_{31} - \frac{1}{2}\theta), & (\frac{1}{2}\theta - a_{31}) \\ a_{41}, & (\frac{1}{2}\theta - a_{43} - a_{41}), & (\frac{1}{2}\theta - a_{41}), & (a_{44} - a_{43} - a_{41} - \frac{1}{2}\theta) \end{vmatrix}.$$

Adding first row to third and fourth we get

$$G = 4 \begin{vmatrix} -\frac{1}{2}\theta, & a_{34}, & (\frac{1}{2}\theta - a_{32}), & (\frac{1}{2}\theta - a_{42}) \\ a_{21}, & -\frac{1}{2}\theta, & (a_{23} - \frac{1}{2}\theta), & (a_{24} - \frac{1}{2}\theta) \\ (a_{31} - \frac{1}{2}\theta), & (\frac{1}{2}\theta - a_{31}), & 0, & (\theta - a_{31} - a_{42}) \\ (a_{41} - \frac{1}{2}\theta), & (\frac{1}{2}\theta - a_{41}), & (\theta - a_{32} - a_{21}), & 0 \end{vmatrix}.$$

Adding second row to first we get :

$$G = 4 \begin{vmatrix} (a_{21}-\frac{1}{2}\theta), & (a_{34}-\frac{1}{2}\theta), & 0, & 0 \\ a_{21}, & -\frac{1}{2}\theta, & (a_{23}-\frac{1}{2}\theta), & (a_{24}-\frac{1}{2}\theta) \\ (a_{31}-\frac{1}{2}\theta), & (\frac{1}{2}\theta-a_{31}), & 0, & (\theta-a_{31}-a_{42}) \\ (a_{41}-\frac{1}{2}\theta), & (\frac{1}{2}\theta-a_{41}), & (\theta-a_{32}-a_{41}), & 0 \end{vmatrix}.$$

Adding second column to first we get :

$$G = 4 \begin{vmatrix} (a_{21}+a_{24}-\theta), & (a_{24}-\frac{1}{2}\theta), & 0, & 0 \\ (a_{21}-\frac{1}{2}\theta), & -\frac{1}{2}\theta, & (a_{23}-\frac{1}{2}\theta), & (a_{24}-\frac{1}{2}\theta) \\ 0, & (\frac{1}{2}\theta-a_{31}), & 0, & (\theta-a_{31}-a_{42}) \\ 0, & (\frac{1}{2}\theta-a_{41}), & (\theta-a_{32}-a_{41}), & 0 \end{vmatrix}.$$

We may take the factor inside the determinant again by multiplying the second row by 2 and the second column by 2.

In the particular case required we have also got

$$a_{31} + a_{24} = a_{32} + a_{41} = a_{31} + a_{42} = \frac{1}{4}\omega.$$

Thus we get

$$G = \begin{vmatrix} (\frac{1}{4}\omega - \theta), & (2a_{24} - \theta), & 0, & 0 \\ (2a_{21} - \theta), & -2\theta, & (2a_{23} - \theta), & (2a_{24} - \theta) \\ 0, & (\theta - 2a_{31}), & 0, & (\theta - \frac{1}{4}\omega) \\ 0, & (\theta - 2a_{41}), & (\theta - \frac{1}{4}\omega), & 0 \end{vmatrix}.$$

$$G = (\frac{1}{4}\omega - \theta) \begin{vmatrix} -2\theta, (2a_{23}-\theta), (2a_{24}-\theta) \\ (\theta-2a_{31}), & 0, (\theta-\frac{1}{4}\omega) \\ (\theta-2a_{41}), (\theta-\frac{1}{4}\omega), & 0 \end{vmatrix} + (\theta-2a_{24})(\theta-2a_{21})(\theta-\frac{1}{4}\omega)^2,$$

$$G = (\theta - \frac{1}{4}\omega)^2 \{ (\theta - 2a_{31})(\theta - 2a_{24}) + (\theta - 2a_{23})(\theta - 2a_{41}) \\ + (\theta - 2a_{34})(\theta - 2a_{21}) - 2\theta(\theta - \frac{1}{4}\omega) \}.$$

Thus

$$G = (\theta - \frac{1}{4}\omega)^2 \{ \theta^2 - \omega\theta + 4(a_{31}a_{24} + a_{23}a_{41} + a_{21}a_{34}) \}$$

or, putting in the values of a_{31} , a_{24} , a_{23} , a_{41} , a_{21} , a_{34} , and ω and making use of the relation

$$\Sigma AB - \Sigma A^2 = 2\Delta^2,$$

we get

$$G = (\theta - \frac{1}{4}\Sigma A)^2 \{ \theta^2 - \frac{3}{4}\Sigma A \cdot \theta + \frac{1}{2}\Delta^2 \}.$$

Equating G to zero we observe that the two equal roots are positive. The other two roots are given by the equation

$$\theta^2 - \frac{2}{3}\Sigma A . \theta + \frac{1}{3}\Delta^2 = 0.$$

But we know that all the roots must be real and so, since the coefficient of θ is here negative and the absolute term is positive it follows that these two roots are also positive.

Thus, since all four roots of the equation $G = 0$ are positive, it follows that the quadratic form :

$$\begin{aligned} Ax_1^2 + Bx_2^2 + Cx_3^2 + Dx_4^2 + (\omega - C - D)x_1x_2 + (\omega - D - A)x_2x_3 \\ + (\omega - D - B)x_3x_1 + (\omega - B - C)x_1x_4 \\ + (\omega - A - C)x_2x_4 + (\omega - B - A)x_3x_4, \end{aligned}$$

where

$$\omega = \frac{2}{3}(A + B + C + D)$$

is positive unless all the x 's are zero, when it vanishes.

Adding on to this

$$\frac{1}{3}(A + B + C + D)(x_1x_2 + x_2x_3 + x_3x_1 + x_1x_4 + x_2x_4 + x_3x_4),$$

we get the product

$$(Ax_1 + Bx_2 + Cx_3 + Dx_4)(x_1 + x_2 + x_3 + x_4),$$

which is therefore always positive provided that

$$x_1x_2 + x_2x_3 + x_3x_1 + x_1x_4 + x_2x_4 + x_3x_4$$

is positive or zero and the x 's are not all zero.

It follows that, under these circumstances,

$$(Ax_1 + Bx_2 + Cx_3 + Dx_4) \quad \text{and} \quad (x_1 + x_2 + x_3 + x_4)$$

must always have the same sign.

But

$$X_1 + X_2 + X_3 + X_4 = (Ax_1 + Bx_2 + Cx_3 + Dx_4)/\Delta.$$

Thus if we use Hermite's Transformation and if Δ be positive, then under these circumstances

$$(X_1 + X_2 + X_3 + X_4) \quad \text{and} \quad (x_1 + x_2 + x_3 + x_4)$$

will have the same sign, while if Δ be negative they will have opposite signs.

If, on the other hand, we use the *Reversed Transformation* and Δ be negative, then

$$(X_1 + X_2 + X_3 + X_4) \quad \text{and} \quad (x_1 + x_2 + x_3 + x_4)$$

will have the same sign, while if Δ be positive they will have opposite signs.

It will be observed that nothing is said as to the relations of the signs of ΣX_1 and Σx_1 when $\Sigma x_1 x_2$ is negative. In this case the Time-Space point is neither *before* nor *after* the origin.

We thus see that in Time-Space theory the *before* and *after* relations may be expressed analytically in a form which is symmetrical with respect to all four co-ordinates.

It will be convenient for purposes of reference to give the expanded forms of the coefficients of x_1, x_2, x_3, x_4 in the expressions for X_1, X_2, X_3, X_4 in Hermite's Transformation. If we write

$$\begin{aligned} X_1 &= b_{11}x_1 + b_{12}x_2 + b_{13}x_3 + b_{14}x_4 \\ X_2 &= b_{21}x_1 + b_{22}x_2 + b_{23}x_3 + b_{24}x_4, \\ X_3 &= b_{31}x_1 + b_{32}x_2 + b_{33}x_3 + b_{34}x_4, \\ X_4 &= b_{41}x_1 + b_{42}x_2 + b_{43}x_3 + b_{44}x_4. \end{aligned}$$

then the expression for b_{11}, b_{12} , etc., are given by the following table :

Let

$$(\lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32}) = w,$$

then

$$\Delta = 1 + 2 \Sigma (\lambda_{34}\lambda_{42} + \lambda_{42}\lambda_{23} + \lambda_{23}\lambda_{34}) - \Sigma \lambda_{pq}^2 - 3w^2.$$

$$\begin{aligned} b_{11} = \frac{1}{\Delta} \{ & (1 + \lambda_{21} + \lambda_{31} + \lambda_{41})^2 + (w + \lambda_{42} + \lambda_{43} + \lambda_{23})^2 \\ & + (w + \lambda_{23} + \lambda_{24} + \lambda_{34})^2 + (w + \lambda_{34} + \lambda_{32} + \lambda_{42})^2 \\ & + 4(\lambda_{23}\lambda_{34} + \lambda_{34}\lambda_{42} + \lambda_{42}\lambda_{23} - \lambda_{23}^2 - \lambda_{34}^2 - \lambda_{42}^2) \}, \end{aligned}$$

$$\begin{aligned} b_{12} = \frac{2}{\Delta} \{ & \lambda_{31}(1 + \lambda_{12} + \lambda_{32} + \lambda_{42} + \lambda_{34} + \lambda_{31}) \\ & + \lambda_{41}(1 + \lambda_{12} + \lambda_{32} + \lambda_{42} + \lambda_{43} + \lambda_{41}) + (2\lambda_{34} + \lambda_{14} + \lambda_{31})w \}, \end{aligned}$$

$$\begin{aligned} b_{13} = \frac{2}{\Delta} \{ & \lambda_{41}(1 + \lambda_{13} + \lambda_{43} + \lambda_{23} + \lambda_{42} + \lambda_{41}) \\ & + \lambda_{21}(1 + \lambda_{13} + \lambda_{43} + \lambda_{23} + \lambda_{24} + \lambda_{21}) + (2\lambda_{42} + \lambda_{12} + \lambda_{41})w \}, \end{aligned}$$

$$\begin{aligned} b_{14} = \frac{2}{\Delta} \{ & \lambda_{21}(1 + \lambda_{14} + \lambda_{24} + \lambda_{34} + \lambda_{23} + \lambda_{21}) \\ & + \lambda_{31}(1 + \lambda_{14} + \lambda_{34} + \lambda_{24} + \lambda_{32} + \lambda_{31}) + (2\lambda_{23} + \lambda_{13} + \lambda_{21})w \}. \end{aligned}$$

$$\begin{aligned}
b_{21} &= \frac{2}{\Delta} \{ \lambda_{42} (1 + \lambda_{21} + \lambda_{31} + \lambda_{41} + \lambda_{43} + \lambda_{42}) \\
&\quad + \lambda_{32} (1 + \lambda_{21} + \lambda_{31} + \lambda_{41} + \lambda_{34} + \lambda_{32}) + (2 \lambda_{43} + \lambda_{23} + \lambda_{42}) w \}, \\
b_{22} &= \frac{1}{\Delta} \{ [(1 + \lambda_{32} + \lambda_{42} + \lambda_{12})^2 + (w + \lambda_{43} + \lambda_{41} + \lambda_{31})^2 \\
&\quad + (w + \lambda_{14} + \lambda_{13} + \lambda_{43})^2 + (w + \lambda_{31} + \lambda_{34} + \lambda_{14})^2] \\
&\quad + 4 (\lambda_{31} \lambda_{43} + \lambda_{43} \lambda_{14} + \lambda_{14} \lambda_{31} - \lambda_{31}^2 - \lambda_{43}^2 - \lambda_{14}^2) \}, \\
b_{23} &= \frac{2}{\Delta} \{ \lambda_{12} (1 + \lambda_{23} + \lambda_{13} + \lambda_{43} + \lambda_{14} + \lambda_{12}) \\
&\quad + \lambda_{42} (1 + \lambda_{23} + \lambda_{13} + \lambda_{43} + \lambda_{41} + \lambda_{42}) + (2 \lambda_{14} + \lambda_{24} + \lambda_{12}) w \}, \\
b_{24} &= \frac{2}{\Delta} \{ \lambda_{32} (1 + \lambda_{24} + \lambda_{34} + \lambda_{14} + \lambda_{31} + \lambda_{32}) \\
&\quad + \lambda_{12} (1 + \lambda_{24} + \lambda_{34} + \lambda_{14} + \lambda_{13} + \lambda_{12}) + (2 \lambda_{31} + \lambda_{21} + \lambda_{32}) w \}. \\
\hline
b_{31} &= \frac{2}{\Delta} \{ \lambda_{23} (1 + \lambda_{31} + \lambda_{41} + \lambda_{21} + \lambda_{24} + \lambda_{23}) \\
&\quad + \lambda_{43} (1 + \lambda_{31} + \lambda_{41} + \lambda_{21} + \lambda_{42} + \lambda_{43}) + (2 \lambda_{24} + \lambda_{34} + \lambda_{23}) w \}, \\
b_{32} &= \frac{2}{\Delta} \{ \lambda_{43} (1 + \lambda_{32} + \lambda_{42} + \lambda_{12} + \lambda_{41} + \lambda_{43}) \\
&\quad + \lambda_{13} (1 + \lambda_{32} + \lambda_{42} + \lambda_{12} + \lambda_{14} + \lambda_{13}) + (2 \lambda_{41} + \lambda_{31} + \lambda_{43}) w \}, \\
b_{33} &= \frac{1}{\Delta} \{ [(1 + \lambda_{43} + \lambda_{13} + \lambda_{23})^2 + (w + \lambda_{24} + \lambda_{21} + \lambda_{41})^2 \\
&\quad + (w + \lambda_{41} + \lambda_{42} + \lambda_{12})^2 + (w + \lambda_{12} + \lambda_{14} + \lambda_{24})^2] \\
&\quad + 4 (\lambda_{41} \lambda_{12} + \lambda_{12} \lambda_{24} + \lambda_{24} \lambda_{41} - \lambda_{41}^2 - \lambda_{12}^2 - \lambda_{24}^2) \}, \\
b_{34} &= \frac{2}{\Delta} \{ \lambda_{13} (1 + \lambda_{34} + \lambda_{14} + \lambda_{24} + \lambda_{12} + \lambda_{13}) \\
&\quad + \lambda_{23} (1 + \lambda_{34} + \lambda_{14} + \lambda_{24} + \lambda_{21} + \lambda_{23}) + (2 \lambda_{12} + \lambda_{32} + \lambda_{13}) w \}. \\
\hline
b_{41} &= \frac{2}{\Delta} \{ \lambda_{34} (1 + \lambda_{41} + \lambda_{21} + \lambda_{31} + \lambda_{32} + \lambda_{34}) \\
&\quad + \lambda_{24} (1 + \lambda_{41} + \lambda_{21} + \lambda_{31} + \lambda_{23} + \lambda_{24}) + (2 \lambda_{32} + \lambda_{42} + \lambda_{34}) w \}, \\
b_{42} &= \frac{2}{\Delta} \{ \lambda_{14} (1 + \lambda_{42} + \lambda_{12} + \lambda_{32} + \lambda_{13} + \lambda_{14}) \\
&\quad + \lambda_{34} (1 + \lambda_{42} + \lambda_{12} + \lambda_{32} + \lambda_{31} + \lambda_{34}) + (2 \lambda_{13} + \lambda_{43} + \lambda_{14}) w \}, \\
b_{43} &= \frac{2}{\Delta} \{ \lambda_{24} (1 + \lambda_{43} + \lambda_{23} + \lambda_{13} + \lambda_{21} + \lambda_{24}) \\
&\quad + \lambda_{14} (1 + \lambda_{43} + \lambda_{23} + \lambda_{13} + \lambda_{12} + \lambda_{14}) + (2 \lambda_{21} + \lambda_{41} + \lambda_{24}) w \}, \\
b_{44} &= \frac{1}{\Delta} \{ [(1 + \lambda_{14} + \lambda_{24} + \lambda_{34})^2 + (w + \lambda_{21} + \lambda_{23} + \lambda_{13})^2 \\
&\quad + (w + \lambda_{32} + \lambda_{31} + \lambda_{21})^2 + (w + \lambda_{13} + \lambda_{12} + \lambda_{32})^2] \\
&\quad + 4 (\lambda_{13} \lambda_{21} + \lambda_{21} \lambda_{32} + \lambda_{32} \lambda_{13} - \lambda_{13}^2 - \lambda_{21}^2 - \lambda_{32}^2) \}. \\
\hline
\end{aligned}$$

It should be observed that, in deriving one of these coefficients, from another by interchange of suffixes, the expression w may be changed into $-w$, but, by reversing the order of the suffixes to certain of the λ 's, we may restore the positive sign.

Thus, for example, in passing from b_{11} to b_{22} the expression

$$(w + \lambda_{42} + \lambda_{43} + \lambda_{23})^2$$

becomes

$$(-w + \lambda_{13} + \lambda_{14} + \lambda_{34})^2.$$

Now reversing the order of the suffixes in λ_{13} , λ_{14} , λ_{34} changes them into $-\lambda_{31}$, $-\lambda_{41}$, $-\lambda_{43}$, so that the latter square may be written in the form

$$(w + \lambda_{43} + \lambda_{41} + \lambda_{31})^2,$$

which is symmetrical with the former.

It will be observed that if $w = 0$ there is a considerable simplification in these coefficients, since both the numerators and the denominator then become quadratic functions of the λ 's. Now there are certain limiting forms of these coefficients which may be obtained in this case.

Let λ_{pq}/f be written for each of the constants λ_{pq} , where f is any constant other than zero and let both the numerators and the denominator be multiplied by f^2 . Now passing to the limit by making f zero we obtain limiting forms of our coefficients b_{11} , b_{12} , etc., which are not, strictly speaking, contained in our general formulæ.

If Δ' be the limiting form taken by the denominator while b_{11}' , b_{12}' , etc., be the limiting forms of the coefficients we have

$$\Delta' = 2 \Sigma (\lambda_{34}\lambda_{42} + \lambda_{42}\lambda_{23} + \lambda_{23}\lambda_{34}) - \Sigma \lambda_{pq}^2,$$

$$b_{11}' = \frac{1}{\Delta'} \{ [(\lambda_{21} + \lambda_{31} + \lambda_{11})^2 + (\lambda_{42} + \lambda_{43} + \lambda_{23})^2 \\ + (\lambda_{23} + \lambda_{24} + \lambda_{34})^2 + (\lambda_{34} + \lambda_{32} + \lambda_{42})^2] \\ + 4(\lambda_{23}\lambda_{34} + \lambda_{34}\lambda_{42} + \lambda_{42}\lambda_{23} - \lambda_{23}^2 - \lambda_{34}^2 - \lambda_{42}^2) \},$$

$$b_{12}' = \frac{2}{\Delta'} \{ \lambda_{31}(\lambda_{12} + \lambda_{32} + \lambda_{42} + \lambda_{34} + \lambda_{31}) \\ + \lambda_{41}(\lambda_{12} + \lambda_{32} + \lambda_{42} + \lambda_{43} + \lambda_{41}) \},$$

with corresponding expressions for the other coefficients and where

$$(\lambda_{12}\lambda_{43} + \lambda_{13}\lambda_{24} + \lambda_{14}\lambda_{32}) = 0.$$

It is clear that, if we call this the *Direct Limiting Transformation* and the corresponding transformation with reversed signs the *Reversed Limiting*

Transformation, then the criteria for the *before* and *after* relations will be similar to those already established, but with Δ' taking the place of Δ .

Symmetrical Form of Wave Equation.

In the following I have written ρ, λ, μ, ν instead of the X_1, X_2, X_3, X_4 on p. 550, so as to avoid unnecessary suffixes.

The wave equation in x, y, z, t co-ordinates may be written in the form

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} - \frac{\partial^2 u}{\partial t^2} = 0.$$

It might have been thought, since the expression for the square of a length in our symmetrical co-ordinates is expressed as a sum of products, that the symmetrical form of the wave equation would involve only mixed partial differential coefficients.

It is found, however, to take the form

$$\sum \frac{\partial^2 u}{\partial \rho^2} - \sum \frac{\partial^2 u}{\partial \rho \partial \lambda} = 0.$$

The corresponding equation for any number of dimensions is found to be

$$\sum \frac{\partial^2 u}{\partial x_p^2} - \frac{2}{n-2} \sum \frac{\partial^2 u}{\partial x_p \partial x_q} = 0,$$

where n is the number of dimensions.

We have

$$\begin{aligned} \frac{\partial u}{\partial x} &= \frac{\partial u}{\partial \rho} \frac{\partial \rho}{\partial x} + \frac{\partial u}{\partial \lambda} \frac{\partial \lambda}{\partial x} + \frac{\partial u}{\partial \mu} \frac{\partial \mu}{\partial x} + \frac{\partial u}{\partial \nu} \frac{\partial \nu}{\partial x} \\ &= \frac{\sqrt{6}}{4} \left(\frac{\partial u}{\partial \rho} + \frac{\partial u}{\partial \lambda} - \frac{\partial u}{\partial \mu} - \frac{\partial u}{\partial \nu} \right), \end{aligned}$$

$$\frac{\partial u}{\partial y} = \frac{\sqrt{6}}{4} \left(\frac{\partial u}{\partial \rho} - \frac{\partial u}{\partial \lambda} + \frac{\partial u}{\partial \mu} - \frac{\partial u}{\partial \nu} \right),$$

$$\frac{\partial u}{\partial z} = \frac{\sqrt{6}}{4} \left(\frac{\partial u}{\partial \rho} - \frac{\partial u}{\partial \lambda} - \frac{\partial u}{\partial \mu} + \frac{\partial u}{\partial \nu} \right),$$

$$\frac{\partial u}{\partial t} = \frac{\sqrt{2}}{4} \left(\frac{\partial u}{\partial \rho} + \frac{\partial u}{\partial \lambda} + \frac{\partial u}{\partial \mu} + \frac{\partial u}{\partial \nu} \right),$$

$$\begin{aligned}
\frac{\partial^2 u}{\partial x^2} &= \frac{1}{8} \left(\frac{\partial^2 u}{\partial \rho^2} + \frac{\partial^2 u}{\partial \rho \partial \lambda} - \frac{\partial^2 u}{\partial \rho \partial \mu} - \frac{\partial^2 u}{\partial \rho \partial \nu} \right) \\
&\quad + \frac{1}{8} \left(\frac{\partial^2 u}{\partial \lambda \partial \rho} + \frac{\partial^2 u}{\partial \lambda^2} - \frac{\partial^2 u}{\partial \lambda \partial \mu} - \frac{\partial^2 u}{\partial \lambda \partial \nu} \right) \\
&\quad - \frac{1}{8} \left(\frac{\partial^2 u}{\partial \mu \partial \rho} + \frac{\partial^2 u}{\partial \mu \partial \lambda} - \frac{\partial^2 u}{\partial \mu^2} - \frac{\partial^2 u}{\partial \mu \partial \nu} \right) \\
&\quad - \frac{1}{8} \left(\frac{\partial^2 u}{\partial \nu \partial \rho} + \frac{\partial^2 u}{\partial \nu \partial \lambda} - \frac{\partial^2 u}{\partial \nu \partial \mu} - \frac{\partial^2 u}{\partial \nu^2} \right), \\
&= \frac{1}{8} \left\{ \frac{\partial^2 u}{\partial \rho^2} + \frac{\partial^2 u}{\partial \lambda^2} + \frac{\partial^2 u}{\partial \mu^2} + \frac{\partial^2 u}{\partial \nu^2} + 2 \frac{\partial^2 u}{\partial \rho \partial \lambda} + 2 \frac{\partial^2 u}{\partial \mu \partial \nu} \right. \\
&\quad \left. - 2 \frac{\partial^2 u}{\partial \rho \partial \mu} - 2 \frac{\partial^2 u}{\partial \lambda \partial \nu} - 2 \frac{\partial^2 u}{\partial \rho \partial \nu} - 2 \frac{\partial^2 u}{\partial \mu \partial \lambda} \right\}.
\end{aligned}$$

Similarly

$$\begin{aligned}
\frac{\partial^2 u}{\partial y^2} &= \frac{1}{8} \left\{ \frac{\partial^2 u}{\partial \rho^2} + \frac{\partial^2 u}{\partial \lambda^2} + \frac{\partial^2 u}{\partial \mu^2} + \frac{\partial^2 u}{\partial \nu^2} + 2 \frac{\partial^2 u}{\partial \rho \partial \mu} + 2 \frac{\partial^2 u}{\partial \lambda \partial \nu} \right. \\
&\quad \left. - 2 \frac{\partial^2 u}{\partial \rho \partial \nu} - 2 \frac{\partial^2 u}{\partial \mu \partial \lambda} - 2 \frac{\partial^2 u}{\partial \rho \partial \lambda} - 2 \frac{\partial^2 u}{\partial \mu \partial \nu} \right\}, \\
\frac{\partial^2 u}{\partial z^2} &= \frac{1}{8} \left\{ \frac{\partial^2 u}{\partial \rho^2} + \frac{\partial^2 u}{\partial \lambda^2} + \frac{\partial^2 u}{\partial \mu^2} + \frac{\partial^2 u}{\partial \nu^2} + 2 \frac{\partial^2 u}{\partial \rho \partial \nu} + 2 \frac{\partial^2 u}{\partial \mu \partial \lambda} \right. \\
&\quad \left. - 2 \frac{\partial^2 u}{\partial \rho \partial \lambda} - 2 \frac{\partial^2 u}{\partial \mu \partial \nu} - 2 \frac{\partial^2 u}{\partial \rho \partial \mu} - 2 \frac{\partial^2 u}{\partial \lambda \partial \nu} \right\},
\end{aligned}$$

while

$$\begin{aligned}
\frac{\partial^2 u}{\partial t^2} &= \frac{1}{8} \left\{ \frac{\partial^2 u}{\partial \rho^2} + \frac{\partial^2 u}{\partial \lambda^2} + \frac{\partial^2 u}{\partial \mu^2} + \frac{\partial^2 u}{\partial \nu^2} + 2 \frac{\partial^2 u}{\partial \rho \partial \lambda} + 2 \frac{\partial^2 u}{\partial \mu \partial \nu} \right. \\
&\quad \left. + 2 \frac{\partial^2 u}{\partial \rho \partial \mu} + 2 \frac{\partial^2 u}{\partial \lambda \partial \nu} + 2 \frac{\partial^2 u}{\partial \rho \partial \nu} + 2 \frac{\partial^2 u}{\partial \mu \partial \lambda} \right\}.
\end{aligned}$$

Thus

$$\begin{aligned}
\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} - \frac{\partial^2 u}{\partial t^2} &= \left\{ \frac{\partial^2 u}{\partial \rho^2} + \frac{\partial^2 u}{\partial \lambda^2} + \frac{\partial^2 u}{\partial \mu^2} + \frac{\partial^2 u}{\partial \nu^2} \right. \\
&\quad \left. - \left(\frac{\partial^2 u}{\partial \rho \partial \lambda} + \frac{\partial^2 u}{\partial \mu \partial \nu} + \frac{\partial^2 u}{\partial \rho \partial \mu} + \frac{\partial^2 u}{\partial \lambda \partial \nu} + \frac{\partial^2 u}{\partial \rho \partial \nu} + \frac{\partial^2 u}{\partial \mu \partial \lambda} \right) \right\},
\end{aligned}$$

and, equating this to zero, we have a symmetrical form of the wave equation :

$$\Sigma \frac{\partial^2 u}{\partial \rho^2} - \Sigma \frac{\partial^2 u}{\partial \rho \partial \lambda} = 0.$$

In order to find the form of the wave equations in n dimensions ($n > 2$) for the case of symmetrical co-ordinates, we observe that the function :

$$u = K (y^2 - y_1^2 - y_2^2 - \dots - y_{n-1}^2)^{-\frac{n-2}{2}}$$

satisfies the partial differential equation :

$$\sum_1^{n-1} \frac{\partial^2 u}{\partial y_p^2} - \frac{\partial^2 u}{\partial y^2} = 0.$$

Now since the co-ordinates $x_1, x_2, \dots, x_n$ are linear homogeneous functions of $y_1, y_2, \dots, y_{n-1}, y$ it follows that there must be a linear homogeneous relation among the second differential coefficients of u with respect to the variables $x_1, x_2, \dots, x_n$.

Taking the arbitrary constant K equal to $\frac{n-1}{2(n-2)}$ and expressing u in these latter co-ordinates it becomes :

$$u = (\Sigma x_p x_q)^{-\left(\frac{n}{2}-1\right)}.$$

Thus

$$\begin{aligned} \frac{\partial u}{\partial x_1} &= -\left(\frac{n}{2}-1\right)(\Sigma x_p x_q)^{-\frac{n}{2}}(\Sigma x_p - x_1), \\ \frac{\partial^2 u}{\partial x_1^2} &= \frac{n}{2}\left(\frac{n}{2}-1\right)(\Sigma x_p x_q)^{-\frac{n}{2}-1}(\Sigma x_p - x_1)^2 \\ &= \frac{n}{2}\left(\frac{n}{2}-1\right)(\Sigma x_p x_q)^{-\frac{n}{2}-1}\{\Sigma x_p^2 - x_1^2 + 2\Sigma x_p x_q - 2x_1(\Sigma x_p - x_1)\}, \end{aligned}$$

with similar expression for $\partial^2 u / \partial x_2^2$, etc.

There are n expressions of this type, and the only linear homogeneous function of them which is a symmetrical function of all the variables is their sum multiplied by any arbitrary constant.

But

$$\Sigma \frac{\partial^2 u}{\partial x_p^2} = \frac{n(n-2)^2}{2}(\Sigma x_p x_q)^{-\frac{n}{2}} + \frac{n(n-1)(n-2)}{4}(\Sigma x_p x_q)^{-\frac{n}{2}-1}(\Sigma x_p^2).$$

Again

$$\begin{aligned} \frac{\partial^2 u}{\partial x_2 \partial x_1} &= -\left(\frac{n}{2}-1\right)(\Sigma x_p x_q)^{-\frac{n}{2}} + \frac{n}{2}\left(\frac{n}{2}-1\right)(\Sigma x_p x_q)^{-\frac{n}{2}-1}(\Sigma x_p - x_1)(\Sigma x_p - x_2) \\ &= -\left(\frac{n}{2}-1\right)(\Sigma x_p x_q)^{-\frac{n}{2}} \\ &\quad + \frac{n}{2}\left(\frac{n}{2}-1\right)(\Sigma x_p x_q)^{-\frac{n}{2}-1}\{\Sigma x_p^2 - x_1^2 - x_2^2 + 2\Sigma x_p x_q + x_1 x_2 \\ &\quad - x_1(\Sigma x_p - x_1) - x_2(\Sigma x_p - x_2)\} \end{aligned}$$

with similar expression for the other mixed differential coefficients of the second order. There are $\frac{1}{2}n(n-1)$ expressions of this type and the only linear homogeneous function of them which is a symmetrical function of all the variables is their sum multiplied by any arbitrary constant. But

$$\Sigma \frac{\partial^2 u}{\partial x_p \partial x_q} = \frac{n(n-2)^2}{4} (\Sigma x_p x_q)^{-\frac{n}{2}} + \frac{n(n-1)(n-2)^2}{8} (\Sigma x_p x_q)^{-\frac{n}{2}-1} (\Sigma x_p^2).$$

This is obviously equal to $\Sigma \frac{\partial^2 u}{\partial x_p^2}$ multiplied by $\frac{n-2}{2}$ and so we find that

$$\Sigma \frac{\partial^2 u}{\partial x_p^2} - \frac{2}{n-2} \Sigma \frac{\partial^2 u}{\partial x_p \partial x_q} = 0.$$

This is a linear homogeneous function of the second differential coefficients of u with respect to the variables $x_1, x_2, \dots, x_n$, which is identically zero and (subject to an arbitrary multiplier) it is clearly the only such function of them which does vanish identically.

The above must therefore be equivalent to what the equation

$$\sum_1^{(n-1)} \frac{\partial^2 u}{\partial y_p^2} - \frac{\partial^2 u}{\partial y^2} = 0$$

becomes when we change from the variables y to the variables x .

For a function v which does not satisfy this differential equation it is important to see whether or no the x operator is equivalent to the y operator multiplied by some constant different from unity, and this may be tested by taking a simple function, say

$$v = y^2.$$

Then

$$\sum_1^{n-1} \frac{\partial^2 v}{\partial y_p^2} - \frac{\partial^2 v}{\partial y^2} = -2.$$

Also

$$v = \frac{n-2}{n} \Sigma x_p^2 + \frac{2(n-2)}{n} \Sigma x_p x_q.$$

Thus

$$\frac{\partial v}{\partial x_1} = \frac{2(n-2)}{n} x_1 + \frac{2(n-2)}{n} (\Sigma x_p - x_1),$$

$$\frac{\partial^2 v}{\partial x_1^2} = \frac{2(n-2)}{n},$$

and

$$\Sigma \frac{\partial^2 v}{\partial x_p^2} = 2(n-2).$$

Also

$$\frac{\partial^2 v}{\partial x_1 \partial x_1} = \frac{2(n-2)}{n},$$

so that

$$\Sigma \frac{\partial^2 v}{\partial x_p \partial x_q} = (n-1)(n-2).$$

Thus

$$\begin{aligned} \Sigma \frac{\partial^2 v}{\partial x_p^2} - \frac{2}{n-2} \Sigma \frac{\partial^2 v}{\partial x_p \partial x_q} &= 2(n-2) - 2(n-1), \\ &= -2, \end{aligned}$$

which is the same as the result given by the y operator and no constant need be introduced.

*Spark Spectra of Bismuth, Bi II and Bi III. Evidence of
Hyperfine Structure.*

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Wave-lengths in the spectrum of a condensed discharge in heated bismuth vapour have been measured from λ 7050 Å. to λ 2000 Å. and those in the spectrum of a condensed spark between metallic terminals in hydrogen from λ 2000 Å. to λ 1340 Å. Hilger E₁ spectrographs, one with a glass and one with a quartz optical system, were used to study the first-mentioned spectral region and a Hilger vacuum fluorite instrument for the latter range. Light from a hot spark between metallic terminals *in vacuo* was photographed with a 1-metre vacuum grating spectrograph in order to investigate the spectrum below λ 1340 Å.

By a study of the frequencies of the wave-lengths thus obtained, considerable progress has been made in the identification of the multiplet term structure of bismuth II and of bismuth III. Confirmation of the correctness of assignment of wave-lengths to one or other of these spectra was obtained readily in most cases by varying the excitation of the sources of light by means of inductance in the secondary spark circuit.

Evidence of hyperfine structure in both spectra was also apparent and the effect was in a few cases of very large magnitude. Such structure is to be

* Mr. Crawford was enabled to participate in this investigation through the award of a Fellowship to him by the National Research Council of Canada.

expected since the bismuth nucleus has a resultant moment of momentum of $4\frac{1}{2} \hbar/2\pi$ according to Back and Goudsmit's interpretation* of fine structure in the spectrum Bi I. Reference may be made to the chapter on this subject in "Structure of Line Spectra" by Pauling and Goudsmit for any theory that is needed in the present discussion.

The results of our investigation of the structure of the spectrum of Bi III are presented below in Tables I and II and of that of Bi II in Tables III and IV. The former is treated first since it is important to know it in order to follow more easily the interpretation of the latter. It might be mentioned at this point that the determination of accurate wave-lengths and the estimation of intensities was found to be very difficult because of the variable broadness of many wave-lengths. This amounted sometimes to several cm^{-1} and is due undoubtedly to unresolved fine structure. The frequencies of wave-lengths are given in the tables, therefore only to the whole wave-number except those of fine structure components, which are quoted to the first decimal place since the intervals between these could be measured fairly well. The terms that have measurable fine structure have been assigned a single value, that is approximately the centroid, in the term tables. The characteristics of the wave-lengths are noted by letters suffixed to the intensity number as explained in the footnotes to Tables II and IV.

Table I.—Terms of Bi III.

Level.	Interval.	n^* .	Level.	Interval.	n^* .
$6p \ ^3P_{1\frac{1}{2}}^\circ$	184390	2.314	$8s \ ^2S_{\frac{1}{2}}$	61054	4.022
$6s6p^3 \ 1_{\frac{1}{2}}$	123143		$7d \ ^3D_{1\frac{1}{2}}$	57095	4.159
$6s6p^3 \ 2_{\frac{1}{2}}$	116943	"	$7d \ ^3D_{2\frac{1}{2}}$	55084	4.234
$7s \ ^2S_{\frac{1}{2}}$	111105	2.982	$6f \ ^3F_{2\frac{1}{2}}^\circ$	43994	4.738
$6d \ ^3D_{1\frac{1}{2}}$	110027	2.996	$6f \ ^3F_{2\frac{1}{2}}^\circ$	43938	4.741
$6d \ ^3D_{2\frac{1}{2}}$	108725	3.086	$5g \ ^2G_{4\frac{1}{2}}$	39946	4.972
$6s6p^3 \ 3_{\frac{1}{2}}$	89765		$5g \ ^2G_{3\frac{1}{2}}$	39943	4.972
$7p \ ^3P_{\frac{1}{2}}^\circ$	89188	3.328	$6g \ ^2G_{4\frac{1}{2}}$	27713	5.970
$7p \ ^3P_{1\frac{1}{2}}^\circ$	84053	3.428	$6g \ ^2G_{3\frac{1}{2}}$	27710	5.970
$5f \ ^3F_{2\frac{1}{2}}^\circ$	68725	3.791	$7h \ ^2H^\circ$	20156	7.000
$5f \ ^3F_{2\frac{1}{2}}^\circ$	68625	3.794			

* 'Z. Physik,' vol. 43, p. 321 (1927) and vol. 47, p. 174 (1928).

Table II.—Classified Wave-lengths of Bi III.

l sum.	I.	λ (I.A.).	ν .	Classification.
5	5	6160.6	16228	$6f^2F_{3\frac{1}{2}}^{\circ} - 6g^2G_{3\frac{1}{2}}$
6	6	6140.4	16281	$6f^2F_{3\frac{1}{2}}^{\circ} - 6g^2G_{4\frac{1}{2}}$
1	1	39.2	16284	$6f^2F_{3\frac{1}{2}}^{\circ} - 6g^2G_{3\frac{1}{2}}$
45	45B	5079.3	19682	$6d^2D_{2\frac{1}{2}} - 7p^2P_{1\frac{1}{2}}$
3	3	52.3	19787	$5g^2G_{3\frac{1}{2}} - 7h^2H^{\circ}$
4	4	51.7	19790	$5g^2G_{4\frac{1}{2}} - 7h^2H^{\circ}$
40	40b	4797.4	20839	$6d^2D_{1\frac{1}{2}} - 7p^2P_{\frac{1}{2}}$
26+	8	52.09	21037.5	$6s6p^2 3_{2\frac{1}{2}} - 5f^2F_{3\frac{1}{2}}$
	6	51.48	21040.2	
	5	50.96	21042.5	
	4	50.50	21044.5	
	3	50.12	21046.2	
10	α			$6s6p^2 3_{2\frac{1}{2}} - 5f^2F_{2\frac{1}{2}}^{\circ}$
	3	29.53	21137.9	
	2	28.95	21140.4	
	2	28.46	21142.6	
	1	28.02	21144.6	
60	2u	27.5	21147	$7s^2S_{\frac{1}{2}} - 7p^2P_{\frac{1}{2}}$
	30	4561.54	21916.3	
	30	60.84	21919.7	
	25	4327.8	23100	
	10	3848.8	25975	
10	10	3708.4	26958	$6d^2D_{1\frac{1}{2}} - 7p^2P_{1\frac{1}{2}}$
100	50	3695.68	27050.9	$7p^2P_{1\frac{1}{2}} - 7d^2D_{1\frac{1}{2}}$
15	50	95.32	27053.6	$7s^2S_{\frac{1}{2}} - 7p^2P_{1\frac{1}{2}}$
35	15	3540.8	28234	$7p^2P_{\frac{1}{2}} - 8s^2S_{\frac{1}{2}}$
40	35	3485.5	28682	$5f^2F_{2\frac{1}{2}}^{\circ} - 5g^2G_{3\frac{1}{2}}$
5	40	73.8	28779	$5f^2F_{3\frac{1}{2}}^{\circ} - 5g^2G_{4\frac{1}{2}}$
40	5	73.4	28782	$5f^2F_{3\frac{1}{2}}^{\circ} - 5g^2G_{3\frac{1}{2}}$
35	40	51.0	28960	$7p^2P_{1\frac{1}{2}} - 7d^2D_{2\frac{1}{2}}$
30	35	3115.0	32093	$7p^2P_{\frac{1}{2}} - 7d^2D_{1\frac{1}{2}}$
	9	3039.86	32886.7	$6s6p^2 2_{2\frac{1}{2}} - 7p^2P_{1\frac{1}{2}}$
	7	39.53	32890.3	
	5	39.25	32893.3	
	4	39.05	32895.6	
	3	38.87	32897.4	
15	2	38.72	32899.0	$6s6p^2 1_{1\frac{1}{2}} - 7p^2P_{\frac{1}{2}}$
	6	2944.46	33952.2	
	4	44.20	33955.2	
	3	43.99	33957.6	
	2	43.84	33959.3	
80	80B	2855.6	35009	$6d^2D_{2\frac{1}{2}} - 5f^2F_{3\frac{1}{2}}$
30	30B	47.4	35109	$6d^2D_{2\frac{1}{2}} - 5f^2F_{2\frac{1}{2}}$
8	8	2443.3	40916	$5f^2F_{2\frac{1}{2}}^{\circ} - 6g^2G_{3\frac{1}{2}}$
10	10	37.6	41012	$5f^2F_{3\frac{1}{2}}^{\circ} - 6g^2G_{4\frac{1}{2}}$
2	2	37.4	41015	$5f^2F_{3\frac{1}{2}}^{\circ} - 6g^2G_{3\frac{1}{2}}$
75	75b	14.6	41402	$6d^2D_{1\frac{1}{2}} - 5f^2F_{2\frac{1}{2}}$
10	3	2184.23	45768.3	$6s6p^2 3_{2\frac{1}{2}} - 6f^2F_{3\frac{1}{2}}$
	2	84.10	45771.1	
	2	84.00	45773.2	
	1	83.92	45774.9	
	1	83.85	45776.3	
	1	83.79	45777.6	

^a Merged with strong Bi II line—see Table IV.^b Broad.^B Very broad, evidence of structure.^u Diffuse.

Table II—(continued).

I sum.	I.	λ (I. A.)	ν .	Classification.
2+	1	81.6	45824	$6s6p^2\ 3^2_2 - 6f^2F^2_{3/2}^\circ$
	1	81.5	45826	
	— ^c			
	14	2073.37	48215.2	
50	10	73.22	48218.7	$6s6p^2\ 2^2_{3/2} - 5f^2F^2_{3/2}^\circ$
	8	73.10	48221.5	
	7	72.99	47224.0	
	6	72.90	48226.1	
	5	72.83	48227.8	
	2	69.08	48315.2	
5+	— ^d			$6s6p^2\ 2^2_{3/2} - 5f^2F^2_{3/2}^\circ$
	1	68.72	48323.6	
	1	68.63	48325.7	
	1	68.55	48327.5	
		λ (I. vac.)		
20	20	1834.32	54516	$6s6p^2\ 1^2_{1/2} - 5f^2F^2_{3/2}^\circ$
50	50 ^u	1606.40	62251	$6p^2P^2_{1/2} - 6s6p^2\ 1^2_{1/2}$
40	40 ^u	1561.02	68445	$0p^2P^2_{1/2} - 6s6p^2\ 2^2_{3/2}$
90	90 ^u	1346.08	74290	$6p^2P^2_{1/2} - 7s^2S^2_{1/2}$
—	— ^e	26.9	75364	$6p^2P^2_{1/2} - 6d^2D^2_{1/2}$
60	60	1224.78	81655	$0p^2P^2_{1/2} - 6d^2D^2_{1/2}$
40	40 ^u	1045.81	95620	$6p^2P^2_{1/2} - 6s6p^2\ 3^2_{2/2}$

^c Four components resolvable but too faint to be observed.

^d Two components merged with strong Bi II line—see Table IV.

^e Wave-length observed and measured by Lang, 'Phil. Trans. Roy. Soc., A, vol. 224, p. 371 (1924); also used in Bi II—see Table IV.

^u Diffuse.

A glance at Tables I and II will show that the simple one-electron doublet spectrum of Bi III has been established to quite an extent. The tables have been made out in conformity with the system proposed by Russell, Shenstone and Turner.* The term values are the absolute ones based on zero at ionisation and were arrived at by assuming $7h^2H$ to be hydrogenic. It was necessary to use absolute values rather than those based on zero for the deepest term since unfortunately this term $6p^2P^2_{1/2}^\circ$ has not been identified. The $6p^2P^\circ$ interval should be about 20,000 cm.^{-1} , either by extrapolation from the mean differences of certain groups of terms in Bi II that indicate jj coupling and have $6p^2P^0$ of Bi III as limit or by extrapolation with the aid of the regular doublet law from Tl I† and Pb II.‡ The value of $6p^2P^2_{1/2}^\circ$ should

* 'Phys. Rev.,' vol. 33, p. 900 (1929).

† Fowler, 'Series in Line Spectra,' 1922.

‡ 'Z. Physik,' vol. 42, p. 265 (1927).

therefore be approximately $205,400 \text{ cm.}^{-1}$ and the ionisation potential 25.4 volts.

The combinations of $6p^2P_{\frac{1}{2}}^{\circ}$ with even terms will lie all below $1300 \text{ \AA}$. The spectrograms obtained by us with the vacuum grating showed that the excitation in the hot spark source was very high. Wave-lengths of Bi II hardly appeared at all and probably only the stronger ones of Bi III were observed. However, the accuracy of measurement on these plates is very poor and it was deemed advisable to postpone any systematic study with some type of controlled excitation of the spark spectrum of bismuth below $\lambda 1340 \text{ \AA}$. till a new 3-metre vacuum grating spectrograph that is now being set up is in working order.

Interesting features of the doublet spectrum of Bi III are the large ^2D and small $^2F^{\circ}$ intervals and the resolution of the ^2G ones as compared, say, with those of the alkali-like spectrum of Tl III.* The $^2F^{\circ}$ and ^2G terms of Bi III are inverted, the ^2D terms normal like those of Tl I.† The inversion of $6d^2D$ of Pb II was reported by Gieseler‡ but it seems probable that his $6d^2D_{2\frac{1}{2}}$ and $6s6p^2^2D_{2\frac{1}{2}}$ terms should be interchanged. This makes the $6d^2D$ separation of Pb II normal with a value of 4164 cm.^{-1} in good agreement with 6292 cm.^{-1} in Bi III. Both these values are extremely large compared to the 82 cm.^{-1} interval of the corresponding term of Tl I.†

Three terms have been identified, and designated $1_{\frac{1}{2}}$, $2_{2\frac{1}{2}}$ and $3_{2\frac{1}{2}}$ in Table I, that comprise a part of the important $6s6p^2$ group. Each has a large total fine structure interval as evidenced by the structure of their combinations, that are recorded in Table II, with odd terms. The large magnitudes are to be expected theoretically because of the presence of the single $6s$ electron in the configuration, that has greater interaction with the nucleus than any other outermost electron in an uncompleted group. The intensities of their combinations indicate that the terms may be $^2D_{1\frac{1}{2}}$, $^2D_{2\frac{1}{2}}$ and $^4P_{2\frac{1}{2}}$ respectively. But since the coupling of the electrons is probably very complex such an interpretation may have little meaning. The advisability of dropping the use of ordinary multiplet notation in such cases has been suggested by Goudsmit.§ We have done so accordingly for the three above-mentioned terms of Bi III and for the terms of Bi II, all of which show that complex coupling occurs.

* 'Proc. Roy. Soc.,' A, vol. 125, p. 50 (1929).

† Fowler, "Series in Line Spectra," 1922.

‡ 'Z. Physik,' vol. 42, p. 265 (1927).

§ 'Phys. Rev.,' vol. 35, p. 1336 (1930).

The doublet spectrum of Bi III compares favourably with that of Sb III* as to general disposition of corresponding multiplets, taking into account the much wider separations in the former. The $6s6p^2$ terms of Bi III are relatively less stable than the $5s5p^2$ ones of Sb III, which is the usual effect observed for states of this type in passing from light to heavy atoms. Fifteen wave-lengths were assigned tentatively to Bi III by Lang† some time ago, but only four appear, according to the present investigation, to be real combinations and correctly classified. The latter are the $7s^2S - 7p^2P^\circ$ and $7p^2P^\circ - 7d^2D_{11}$ transitions.

The structure of the two-electron spectrum of Bi II has been interpreted satisfactorily on the basis that almost complete jj coupling occurs between the electrons. The limit at ionisation is $6p^2P^\circ$ of Bi III. The terms in Table III have been designated in a way to show the J values and the odd or even

Table III.—Terms of Bi II.

Level.			Type ?	Level.			Type ?
$6p_{\frac{1}{2}} 6p_{\frac{1}{2}}$	1_0	0	$^2P_0$	$6p_{\frac{1}{2}} 7p_{\frac{1}{2}}$	8_1	88559	$^2D_1$
$6p_{\frac{1}{2}} 6p_{\frac{3}{2}}$	2_1	13322	$^2P_1$	$6p_{\frac{1}{2}} 7s$	9_2°	88763	$^2P_2^\circ$
$6p_{\frac{3}{2}} 6p_{\frac{1}{2}}$	3_2	17025	$^2P_2$	$6p_{\frac{3}{2}} 7p_{\frac{1}{2}}$	9_3	88781	$^2D_3$
$6p_{\frac{3}{2}} 6p_{\frac{3}{2}}$	4_2	33930	$^1D_2$	$6p_{\frac{3}{2}} 7s$	10_1°	89877	$^1P_1^\circ$
$6p_{\frac{1}{2}} 6p_{\frac{1}{2}}$	5_0	44106	$^1S_0$	$6p_{\frac{3}{2}} 5f_{\frac{5}{2}}$	10_2	105077	$^2F_5$
$6p_{\frac{1}{2}} 7s$	1_0°	69126	$^2P_0^\circ$	$6p_{\frac{1}{2}} 7p_{\frac{3}{2}}$	11_2	105263	$^2P_2$
$6p_{\frac{3}{2}} 7s$	2_1°	69590	$^2P_1^\circ$	$6p_{\frac{3}{2}} 5f$	12_3	105281	$^2F_3$
$6s 6p^2$	3_1°	69590	$^4S_2^\circ$ or $^2S_1^\circ$	$6p_{\frac{1}{2}} 5f$	13_3	105443	$^2G_3$
$6s 6p^2$	4_2°	76143	$^2D_2^\circ$	$6p_{\frac{3}{2}} 5f_{\frac{3}{2}}$	14_4	105720	$^2G_4$
$6p_{\frac{1}{2}} 6d_{\frac{1}{2}}$	5_2°	79083	$^2D_2^\circ$	$6p_{\frac{1}{2}} 7p_{\frac{1}{2}}$	15_1	106441	$^2S_1$
$6p_{\frac{1}{2}} 6d_{\frac{3}{2}}$	6_1°	80569	$^2D_1^\circ$	$6p_{\frac{1}{2}} 7p_{\frac{3}{2}}$	16_3	108272	$^2D_3$
$6p_{\frac{3}{2}} 6d_{\frac{1}{2}}$	7_2°	82041	$^2F_5^\circ$	$6p_{\frac{3}{2}} 8p_{\frac{1}{2}} ?$	17_1	108398	$^2P_1$
$6p_{\frac{3}{2}} 6d_{\frac{3}{2}}$	8_2°	82249	$^2F_3^\circ$	$6p_{\frac{1}{2}} 7p_{\frac{1}{2}}$	18_1	109097	$^1P_1$
$6p_{\frac{1}{2}} 7p_{\frac{1}{2}}$	6_1	84273	$^2P_1$	$6p_{\frac{1}{2}} 7p_{\frac{1}{2}}$	19_3	109897	$^1D_2$
$6p_{\frac{3}{2}} 7p_{\frac{1}{2}}$	7_0	87070	$^2P_0$	$6p_{\frac{1}{2}} 7p_{\frac{1}{2}}$	20_0	110924	$^1S_0$

character only. The configurations are given with the " j " values of each electron added when these could be established with any certainty. Suggested term types are included in another column of the table but are not considered to have much significance in view of the type of vector coupling that prevails. The values of terms are based on a value zero for the deepest one. The groups of terms of the $6p7s$ and $6p7p$ configurations are each divided into two sub-

* Lang, 'Phys. Rev.,' vol. 35, p. 445 (1930). (It should be pointed out that the terms designated by Lang as $5f^2F^\circ$ are actually the $4f^2F^\circ$ ones and his so-called $4f^2F^\circ$ terms are without doubt unreal.)

† 'Phys. Rev.,' vol. 32, p. 737 (1928).

groups with a mean difference between groups of about 20,000 cm.⁻¹. This then is approximately the doublet separation of the 6p electron and was used to estimate the 6p ²P° interval of Bi III as noted before.

Table IV.—Classified Wave-lengths of Bi II.

I sum.	L.	λ (I. A.).	ν.	Classification.
50	50B	8808.6	14683	2 ₁ [°] — 6 ₁ ; 3 [°] — 6 ₁
40	40B	8600.2	15147	1 ₀ [°] — 6 ₁
10	10	6577.2	15200	10 ₁ [°] — 10 ₂
15	15	6497.7	15386	10 ₁ [°] — 11 ₂
15	15	6128.0	16314	9 ₂ [°] — 10 ₂
15	15	6059.1	16500	9 ₂ [°] — 11 ₂
5	5	52.3	16518	9 ₂ [°] — 12 ₂
8	8	35.6	16564	10 ₁ [°] — 15 ₁
40	22b	5719.8	17478	} 2 ₁ [°] — 7 ₀ ; 3 [°] — 7 ₀ ?
	18b	18.6	17482	
20	20	5655.2	17678	
10	10	5397.8	18521	10 ₁ [°] — 17 ₁
	18	5271.07	18966.2	} 2 ₁ [°] — 8 ₁ ; 3 [°] — 8 ₁
40	10	70.34	18968.8	
	12	69.71	18971.1	
	40b	09.7	19189	} 2 ₁ [°] — 9 ₂ ; 3 [°] — 9 ₂
75	35b	08.8	19193	
20	20	01.5	19220	
60	60b	5144.3	19434	10 ₁ [°] — 18 ₁
50	50b	24.3	19509	1 ₀ [°] — 8 ₁
10	10	5091.6	19635	9 ₂ [°] — 16 ₂
20	20a	4993.6	20020	9 ₂ [°] — 17 ₁
10	10	16.6	20334	10 ₁ [°] — 19 ₂
20	20	4749.7	21048	9 ₂ [°] — 18 ₁
30	30	30.3	21134	10 ₁ [°] — 20 ₀
12	12u	4379.4	22828	9 ₂ [°] — 19 ₂
25	25b	40.5	23032	8 ₂ [°] — 10 ₂
12	12b	39.8	23036	8 ₂ [°] — 12 ₂
8	8	10.3	23194	7 ₂ [°] — 10 ₂
3	3	05.4	23220	8 ₂ [°] — 13 ₂
70	70B	01.7	23240	7 ₂ [°] — 11 ₂
25	25	4272.0	23402	7 ₂ [°] — 12 ₂
75	75b	59.4	23471	7 ₂ [°] — 13 ₂
10	10	4097.2	24400	8 ₂ [°] — 14 ₂
40	40b	79.1	24508	7 ₂ [°] — 15 ₁
2	2	48.4	24694	6 ₂ [°] — 10 ₂
3	3U	3931.9	25426	6 ₁ [°] — 11 ₂
30	30	3863.9	25873	5 ₀ [°] — 2 ₁ [°] ; 5 ₀ [°] — 3 [°] ?
10	10	3845.8	25995	0 ₁ [°] — 15 ₁
5	5	41.6	26023	5 ₂ [°] — 10 ₂
3	3	18.6	26180	8 ₂ [°] — 10 ₂
20	20	15.8	26190	5 ₂ [°] — 11 ₂
12	12	11.1	26232	5 ₂ [°] — 12 ₂
5	5c	3793.0	26357	7 ₂ [°] — 16 ₂
70	70b	92.5	26360	7 ₂ [°] — 17 ₁
				5 ₂ [°] — 13 ₂

a Merged with faint fine structure component of Bi III line—see Table II.

b Broad.

B Very broad, evidence of structure.

c Possibly a diffraction edge of λ 3792.5.

u Diffuse.

U Very diffuse.

Table IV—(continued).

I sum.	I.	λ (I.A.).	ν .	Classification.
—	— <i>d</i>	(3695.0)	(27056)	$7_1^\circ - 18_1$
12	12	3654.2	27358	$5_1^\circ - 15_1$
2	2	15.8	27649	$8_2^\circ - 19_2$
2	2 <i>u</i>	3592.4	27829	$6_1^\circ - 17_1$
	5	3455.28	28033.0	
12	3	55.01	28035.2	
	2	54.82	28036.8	$4_2^\circ - 10_2$
	2 <i>u</i>	54.5	28039	
	12	31.23	29135.7	
	10	30.83	29139.1	
40	8	30.53	29141.7	$4_2^\circ - 12_2$
	6	30.30	29143.6	
	4	30.10	29145.3	
4	4U	11.8	29302	$4_2^\circ - 13_2$
2	2 <i>u</i>	10.1	29316	$5_1^\circ - 17_1$
4	4 <i>u</i>	08.6	29329	$6_1^\circ - 19_2$
3	3 <i>u</i>	3330.5	30017	$5_2^\circ - 18_1$
	4	3299.79	30296.3	
10	3	99.57	30298.3	$4_2^\circ - 15_1$
	3U	99.3	30301	
	5	3111.67	32127.8	
	4	11.41	32130.5	
15	3	11.20	32132.6	$4_2^\circ - 16_2$
	2	11.02	32134.5	
	1	10.88	32136.0	
8	8U	3033.5	32956	$4_2^\circ - 18_1$
2	2U	2961.5	33757	$4_2^\circ - 19_2$
	5	2817.36	35483.8	
10	2	17.17	35486.2	$2_1^\circ - 10_2; 3^\circ - 10_2$
	3	17.01	35488.2	
	11	03.70	35656.7	
35	9	03.58	35658.2	$4_2 - 2_1^\circ; 4_2 - 3^\circ$
	15	03.42	35660.2	
2	2U	02.6	35671	$2_1^\circ - 11_2; 3^\circ - 11_2$
1	1 <i>u</i>	01.2	35688	$3_1^\circ - 12_2?$
9	5	2746.36	36401.1	
	4 <i>u</i>	46.2	36403	$5_2 - 6_1^\circ$
1	1 <i>u</i>	2584.6	36679	$3^\circ - 16_2?$
3	3	45.6	39272	$1_6^\circ - 17_1$
	3	30.56	39505.1	
7	2	30.41	39507.4	$2_1^\circ - 18_1; 3^\circ - 18_1$
	2	30.28	39509.4	
10	10	01.0	39972	$1_6^\circ - 18_1$
	2	2480.25	40306.3	
5	1	80.12	40308.5	$2_1^\circ - 19_2; 3^\circ - 19_2$
	2	80.03	40309.9	
2	2U	18.6	41334	$2_1^\circ - 20_0; 3^\circ - 20_0?$
	8	2368.54	42207.2	
	9	68.46	42208.6	
55	10	68.37	42210.2	$4_2 - 4_2^\circ$
	12	68.25	42212.3	
	16	68.12	42214.7	
40	40 <i>b</i>	2214.0	45153	$4_2 - 5_2^\circ$
60	60	2186.9	45712	$5_2 - 10_1^\circ$

b Broad.*d* Probably very faint and unseparated from λ 3695.3 of Bi III.*u* Diffuse.

U Very diffuse.

Table IV—(continued).

I sum.	I.	λ (I.A.).	ν .	Classification.	
40	{	15	43.46	{	$4_2 - 6_1^\circ$
		15	43.40		
		10	43.35		
8		8	2077.8		
45	45b, e	68.9	48112	$4_2 - 7_2^\circ$	
			48319	$4_2 - 8_2^\circ$	
		λ (I. vac.).			
100	100U	1902.42	52565	$3_2 - 2_1^\circ$; $3_2 - 3^\circ$	
80	80	1823.80	54831	$4_2 - 9_2^\circ$	
70	70	1791.93	55806	$2_1 - 1_0^\circ$	
80	80	87.47	55945	$4_2 - 10_1^\circ$	
90	90u	77.13	56270	$2_1 - 2_1^\circ$; $2_1 - 3^\circ$	
20	20U	1691.48	59120	$3_2 - 4_2^\circ$	
80	80	11.38	62059	$3_2 - 5_2^\circ$	
70	70b	1591.76	62820	$2_1 - 4_2^\circ$	
40	40	73.70	63545	$3_2 - 6_1^\circ$	
60	60	38.09	65016	$3_2 - 7_2^\circ$	
80	80U	33.21	65223	$3_2 - 8_2^\circ$	
40	40	20.66	65761	$2_1 - 5_2^\circ$	
50	50	1487.09	67245	$2_1 - 6_1^\circ$	
80	80u	55.23	68718	$2_1 - 7_2^\circ$	
60	60U	36.98	69590	$1_0 - 2_1^\circ$; $1_0 - 3^\circ$?	
50	50	1393.98	71737	$3_2 - 9_2^\circ$	
30	30	72.65	72852	$3_2 - 10_1^\circ$	
—	—f, g	26.9	75364	$2_1 - 9_2^\circ$	
—	—f	06.3	76552	$2_1 - 10_1^\circ$	
—	—f	1241.0	80580	$1_0 - 6_1^\circ$	

b Broad.

e Merged with two faint fine structure components of Bi III line—see Table II.

f Wave-length observed and measured by Lang, Phil. Trans., A, vol. 224, p. 371 (1924).

g Also used in Bi III—see Table II.

u Diffuse.

U Very diffuse.

One term, namely 4_2° of the $6s6p^2$ group, has been located without doubt, since it has a large total fine structure interval like those of the $6s6p^2$ terms of Bi III. Another one that is designated 3° is apparently practically coincident with $6p7p2_1^\circ$ and could not be separated from it. But the correctness of this conclusion is supported strongly by the observed irregular fine structure patterns of the lines that involve the two terms and by the large intensities of certain of these. It is not certain whether the fine structure is due to 2_1° or 3° but it seems as if one term is triple and the other probably unresolved. The two terms have been assigned the same value till a differentiation can be effected.

A few of the constant frequency differences between lines of Bi II that are classified in Table IV were reported correctly some years ago by Ruark, Mohler,

Foote and Chenault,* but they were not able to interpret them at that time.

As to the hyperfine structure problem, the present observations of structure in bismuth spark lines are probably not of much value. The structures recorded in Tables II and IV are each due to the large intervals of one term and smaller unresolved intervals of the other one involved in the transition. Thus each observed component is still complex. This explains the lack of agreement of the large term separations if calculated directly from the line component intervals.

The resolution of the $7s\ ^2S$ term and the three $6s6p^2$ terms of Bi III and of the $6s6p^3\ 4_2^\circ$ term of Bi II each into $2J + 1$ components is consistent with the value $4\frac{1}{2} \hbar/2\pi$ of the moment of momentum of the bismuth nucleus and the separations in the more complex line patterns indicate that the Landé interval rule is fairly well obeyed.

It is most important to know the hyperfine structure of as many terms as possible of the doublet spectrum of Bi III since existing theories of the effect of nuclear angular momentum on a single electron could be applied to them and checked. Only the $7s\ ^2S$ term interval can be evaluated at present. Its magnitude is about 3 or 4 cm.^{-1} but it should be obtained more accurately together with those of other doublet terms. A special investigation into this problem is being projected now.

* 'Sci. Pap. Bur. Standards,' vol. 19, p. 463 (1924).

The Displacement by Ultra Violet Light of the Explosion Limit in a Chain Reaction.

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Mixtures of phosphine and oxygen at the ordinary temperatures do not react appreciably in the course of several days if the pressure is respectively above or below one of two critical values.* If the pressure is between these values the gases explode with a bright flash. This behaviour can be explained by assuming that the oxidation is a chain reaction.† The lower limiting pressure is that at which chains begin to multiply more rapidly than they are broken by the walls of the vessel, as shown by the fact that p_0 , p_{RH} , at this point is inversely proportional to the square of the diameter of the cylindrical containing tube. The upper limiting pressure is that at which the deactivation in the gas phase becomes great enough to prevent the chains from multiplying, and is independent of the diameter of the tube. Moreover the oxygen rather than the phosphine is the principal deactivating agent. In a tube of diameter 2 cm., and with an equimolecular mixture, the lower critical pressure is of the order of 1 to 2 mm.; the upper critical pressure would be about 0.2 atmosphere.

Dalton discovered that if a stable mixture above the upper limiting pressure is exposed to ultra-violet light a rapid but non-explosive interaction occurs; and that suitable illumination thus provides a means of controlling the initial process upon which the development of the chains depends. It seems, therefore, that an investigation of the manner in which the critical explosion limits are influenced by ultra-violet light might lead to a deeper understanding of the mechanism of chain propagation. The present paper deals with the lower pressure limit.

The apparatus used was that described by Dalton and Hinshelwood, the only difference being that the cylindrical reaction tube was of quartz instead of glass. The principle is that the gases are mixed at low pressure and compressed until a flash occurs. The walls of the tube were covered with a thin

* van't Hoff, "Etudes de Dynamique Chimique"; van der Stadt, 'Z. Physik. Chem.', vol. 12, p. 322 (1893); Dalton and Hinshelwood, 'Proc. Roy. Soc.,' A, vol. 125, p. 294 (1929); Dalton, *ibid.*, vol. 128, p. 263 (1930); Trautz and Gabler, 'Z. Anorg. Chem.', vol. 180, p. 321 (1929).

† Dalton and Hinshelwood, *loc. cit.*

layer of syrupy phosphoric acid as before to ensure as constant a surface as possible. The source of light was a quartz mercury lamp.

When illuminated the gases explode at a lower pressure than normally. The increased sensitiveness of the mixture persists after the light is cut off, but gradually decays, as the following figures show.

Ratio of phosphine to oxygen = 0.34 ; silica tube 1.6 cm. diameter, walls wetted with phosphoric acid.

Critical pressure of illuminated mixture = 2.68 mm.

Critical pressure in the light after 3 minutes' illumination = 1.64 mm.

Time allowed for decay in the dark.		Critical pressure,
'	"	mm.
0	0	1.64
0	29	2.01
1	15	2.21
2	30	2.38
4	40	2.53
9	10	2.65
10	0	2.68

(It should be noted that although the absolute values of the pressures given depend on the calibration of the apparatus by the use of a McLeod gauge, the relative values depend simply on the reading of a graduation on the reaction tube.)

The increased explosibility caused by illumination thus appears to be due to the production of a definite substance which has an appreciable time of survival.

In the light there must be a photostationary state : for a constant pressure and light intensity this substance is formed by the light at a rate A , and decays at a rate which will almost certainly be proportional to its amount. It accumulates till its concentration X_0 is such that

$$dX/dt = A - kX_0 = 0.$$

The rate of formation in the light will be expressed by the equation,

$$dX/dt = A - kX,$$

whence

$$X/X_0 = 1 - e^{-kt}$$

while the decay in the dark will be represented by

$$-dX/dt = kX,$$

whence

$$X/X_0 = e^{-kt}$$

It is to be noted that the *decay* constant occurs in each formula, the two corresponding curves being symmetrical.

This gradual formation of the active substance was observed experimentally in two ways. The first was by exposing the mixture to light and then compressing to the explosion point, the total time of illumination, including the period of time required for the compression, being measured with a stop-watch. The second method was to compress the gases first to some suitable pressure and then to illuminate, when an explosion would occur after a definite interval of time which could be recorded. The lower the compression the longer was the time required. This method is in principle subject to the disadvantage that the pressure at which the illumination occurs varies from experiment to experiment, but practically the error introduced is small and the two methods give nearly the same result. The diagrams show two pairs of curves which represent respectively the formation and decay of the active substance. The ordinates represent not the pressure but the actual scale readings of the graduated tube, a high reading representing a low explosion pressure, *i.e.*, a large concentration of the active substance. Fig. 1 and fig. 2 refer to different tubes with different arbitrary scales. The formation curve

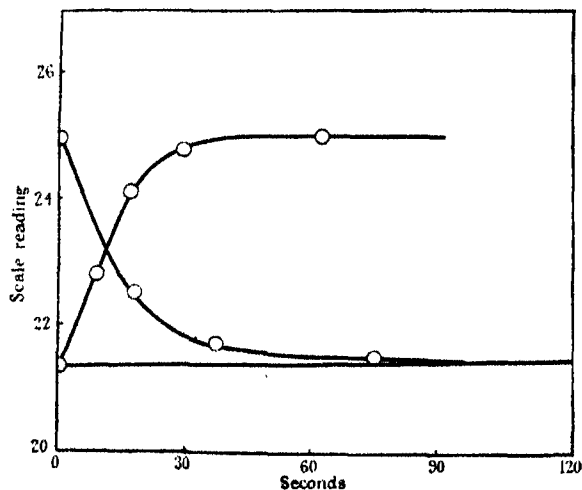


FIG. 1.—Formation and Decay of the Active Substance (Tube 1).

in fig. 1 was obtained by the first method, that in fig. 2 by the second method. The decay curves were obtained with mixtures which had been first illuminated

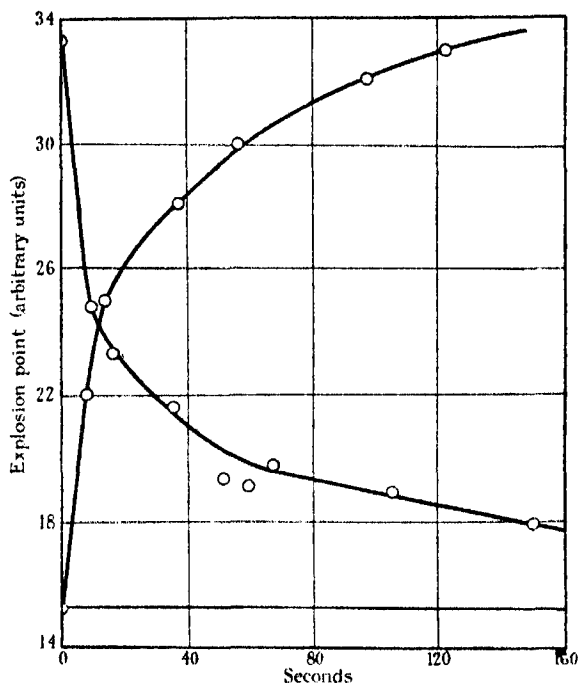


FIG. 2.—Formation and Decay of the Active Substance (Tube 2).

for $1\frac{1}{2}$ and 3 minutes respectively, these times being long enough for the maximum increase in sensitivity to have occurred.

Consideration of the curves leaves little doubt that a stationary state is set up in the light, a definite concentration of some substance being established which makes the phosphine-oxygen mixture more explosible than normally. The action of this substance is thus comparable with that of a trace of nitrogen peroxide on the combination of hydrogen and oxygen.

Since an illuminated mixture returns almost exactly to its original condition after the active substance has decayed in the dark, it is evident that the actual rate of consumption of phosphine and oxygen must have been negligibly small. To obtain information about this rate experiments were made with much more prolonged exposures to light. With a ratio of phosphine to oxygen of approximately 3 to 1 the explosion pressure was 2.62 mm. in the dark. After illumination for 1 hour, and then standing in the dark for 7 minutes for the active substance to decay, the gases had to be compressed to

a volume which would have corresponded to a pressure of 3.12 mm. had none been used up. Assuming that the oxidation in excess of oxygen has occurred according to the equation $\text{PH}_3 + 2\text{O}_2 = \text{H}_3\text{PO}_4$, and remembering that at the critical pressure $p_{\text{PH}_3} \cdot p_{\text{O}_2} = \text{constant}$, it is easy to calculate from the above result that approximately 18.5 per cent. of the phosphine was used up during the hour. A second experiment over a 3-hour interval gave a rate, assumed linear, of 20 per cent. per hour. The assumption of a different equation for the oxidation of the phosphine does not alter the general character of the result. Thus in the 3 minutes' exposures which were usually given, less than 1 per cent. of the phosphine was used up. Thus the return to nearly the original condition after the active substance has decayed in the dark is explained.

If we make the natural, though as yet unproven assumption that each molecule of phosphine under the influence of the light gives one molecule of the active substance, which in turn is destroyed giving ultimately the final oxidation product, we can use the equation $A - kX_0 = 0$ to calculate the concentration, X_0 , in the stationary state. With 0.65 mm. phosphine and 1.97 mm. of oxygen, 0.12 mm. of the phosphine disappear per hour, *i.e.*, 0.33×10^{-4} mm. per second. Under these conditions the experimentally found half-life of the active substance in the dark is about 10 seconds, whence $k = 0.69 \times 10^{-1}$. Therefore $X_0 = 0.33 \times 10^{-4} \div 0.69 \times 10^{-1} = 0.48 \times 10^{-3}$, or 0.07 per cent. of the phosphine pressure.

Experiments were made to determine the influence of the ratio of oxygen to phosphine and of the diameter of the tube on the rate of decay of the active substance; but it soon became evident that this varied so much with the exact state of the walls that such investigations would yield rather uncertain results. The age and strength of the phosphoric acid covering the walls appeared to influence the decay, and on one occasion when the phosphoric acid, having crystallised, had been melted by heating the evacuated tube, the rate of decay was abnormally high for a day, while many experiments were made in the tube.

These results suggest, if they do not prove, that the decay of the active substance occurs on the walls of the vessel, just as the reaction chains are broken at the wall in the dark reaction. Whether the same substance is concerned in each case can not definitely be decided.

It should be mentioned that in one series of experiments in which a fresh reaction tube was installed with new phosphoric acid the rate of decay was too great to measure. Simultaneously the maximum increase of explosiveness

of the mixture was abnormally small, but established nearly immediately, and, what is more significant, the rate at which phosphine was actually used up was abnormally high. This was shown by the fact that the compression required for explosion, instead of returning to the "dark" value, as it normally did, became greater than normal after quite short periods of illumination. This abnormal behaviour is shown by the following numbers :—

Explosion point (scale units).		
"Blank" experiment	13.5	Stationary state established abnormally rapidly.
Compressed in light, time of illumination—		
14"	17.2	
41"	16.9	
1' 25"	16.9	
3' 0"	16.8	

After complete decay in dark, having been exposed to light for—

15"	13.3	Phosphine had been rapidly used up in the light.
100"	12.5	
600"	10.7	

This behaviour allows a conclusion about the nature of the stationary state established in the light. It will appear later that it is the phosphine which is activated. The formation and decay of the active substance may therefore be represented either by (1) $\text{PH}_3 \rightarrow \text{X}$, $\text{X} \rightarrow \text{PH}_3$ or by (2) $\text{PH}_3 \rightarrow \text{X}$, $\text{X} \rightarrow$ products of oxidation. Since a rapid establishment of the stationary state is now found to be associated with a rapid consumption of phosphine mechanism (2) rather than (1) is indicated.

If the active substance is destroyed at the wall it is of interest to enquire what fraction of the collisions which its molecules make with the wall leads to destruction. The calculation may be made as follows.

Let ρ be the concentration of the active substance at a distance r from the axis of the cylindrical tube. ρ is assumed to fall only as a result of the diffusion of the substance to the wall. Then, if C is the coefficient of diffusion

$$C \left(\frac{\partial^2 \rho}{\partial r^2} + \frac{1}{r} \frac{\partial \rho}{\partial r} \right) = \frac{\partial \rho}{\partial t}.$$

The solution* in terms of Bessel functions is

$$\rho = A_1 J_0(\mu_1 r) e^{-\mu_1^2 C t} + A_2 J_0(\mu_2 r) e^{-\mu_2^2 C t} + \dots$$

If nearly all the collisions with the wall are effective we must have $\rho = 0$, when $r = a$, where a is the radius. Also $\rho = \rho_0$ when $t = 0$. Therefore $\mu_1, \mu_2 \dots$ are the roots of the equation

$$J_0(\mu a) = 0 \quad \text{and} \quad A_k = \rho_0 \left[\frac{2}{\mu_k \cdot a \cdot J_1(\mu_k a)} \right].$$

Numerical solution of these equations with the aid of tables shows that with a reasonable diffusion coefficient the decay period would be about 10^4 times smaller than that observed normally. Thus only a small fraction of the collisions is effective. Therefore for a boundary condition we have instead of $\rho = 0$, the relation $C \frac{\partial \rho}{\partial r} + k_1 \rho = 0$ where $k_1 \rho$ is the amount destroyed per square centimetre of the surface in unit time. In these circumstances the values of $\mu_1, \mu_2 \dots$ are the roots of the equation

$$\mu a J_1(\mu a) - a h J_0(\mu a) = 0,$$

where

$$h = k_1 / C$$

and

$$A_k = \rho_0 \left[\frac{2 a h}{(a^2 h^2 + \mu_k^2 a^2) J_0(\mu_k a)} \right].$$

Numerical trials soon show that in the present problem the first term of the series is enough, and also that the values of the Bessel functions are such that we may expand simply by writing $J_0(x) = 1 - x^2/2^2$ and $J_1(x) = x/2$.

Let α be the fraction of the collisions with the wall which destroy the active product. Then since the number of gram molecules striking 1 sq. cm. of surface per second is $\frac{1}{4} \rho \bar{u}$ we must have $k_1 \rho = \frac{1}{4} \alpha \rho \bar{u}$ where $\bar{u}$ is the root mean square velocity.

We assume the following numerical values $a = 0.8$ cm.; $C = 100$ (since the pressure is about 2 mm. and C at atmospheric pressure would be about 0.3); $\bar{u} = 2 \times 10^4$. Knowing the half-life of the active substance we can find α by trial or, with the approximations introduced above, by direct solution. The result is approximately 10^{-5} . We invert the process and calculate the time of decay with this value of α

$$k_1 = \frac{1}{8} \times 10^{-5} \times 2 \times 10^4 = 3.3 \times 10^{-2}.$$

Therefore

$$h = 3.3 \times 10^{-4}.$$

* See for example, Byerly, "Spherical Harmonics," Chapter VII.

Solving the equation we now obtain for the case where $\rho/\rho_0 = 0.5$ the value $t = 8.5$ seconds. This is of the order actually observed in the 1.6 cm. diameter tube as shown in fig. 1.

Thus we conclude that in so far as the active substance is destroyed only at the walls one collision in about 10^5 is effective. It is evident, therefore, that there is much room for variation in the effectiveness of the wall. This is quite in keeping with experiments on the decay of active nitrogen and hydrogen.

To determine what range of wave-lengths were effective, experiments were made with various filters and screens, the results being as follows :—

Filter.	Explosion pressure observed. mm.
Completely opaque metal screen	3.14 ; 3.03
Vita glass transmitting $\lambda > 2900$	3.03 ; 3.03
Chlorine-bromine filter with 40 to 50 per cent. transmission between 2500 and 2800	2.50
Unfiltered light	1.90 ; 1.96

Having regard to the actual lines of the mercury arc and the transmission of the chlorine bromine filter, it is clear that the active wave-lengths lie between 2500 and 2800 Å. Thus $Nh\nu$ lies between about 100,000 and 115,000 calories.

The fact that under normal conditions the activity induced by light persists enables us to illuminate each gas separately and then rapidly to add the other and compress, and thus attempt to find which is activated by the light. The result found is that illumination of the tube alone has no effect, eliminating the phosphoric acid as a source of the active body, with oxygen there is no effect, with phosphine alone there is an appreciable effect, but not nearly so great as with the mixture. The following are some typical results :—

	Explosion point (arbitrary units of the graduated tube).
" Blank experiment " (no illumination) ..	13.3
Empty tube illuminated	13.1
Oxygen illuminated	13.4
Phosphine illuminated	14.7
Mixture illuminated	17.6

(in each case there had to be a decay period of about 30 seconds in the dark).

The activity induced in the phosphine alone decays in a short time, just as

that of the mixture does. The result suggests that the phosphine molecule itself is directly activated by the light; this would also be expected from the effective wave-length. The energy available, 100,000 calories, is probably of about the right magnitude to cause the dissociation $\text{PH}_3 \rightarrow \text{PH}_2 + \text{H}$. The much greater efficacy of illuminating the mixture, however, shows that oxygen also plays an important part in the process, either by combining with the primarily activated phosphine to give the active substance, or by preserving the activated phosphine from some independent decay, such as diffusion to the wall. Attempts to determine the time of decay of the phosphine activity were difficult owing to the small magnitude of the effect and the rapidity of the decay itself. By adding nitrogen it was hoped to increase the life by diminishing diffusion. In one series of experiments 5 parts of nitrogen, 1 of phosphine and 3 of oxygen were all illuminated, and the half-life of the activity was found to be 20 seconds. When the nitrogen and phosphine alone were illuminated, the oxygen being added subsequently, the half-life of the much smaller activity was about 7 seconds only. Evidently, therefore, the oxygen has an influence which is not merely due to its contribution to the total pressure.

In discussion of chain reactions the question often arises whether the chain is an "energy" chain or a "material" chain. There appears to be little doubt that in this reaction a material chain is concerned. That the same is therefore true for the dark reaction does not necessarily follow, but possesses a certain degree of probability.

Summary.

Mixtures of phosphine and oxygen at ordinary temperatures react negligibly slowly except between two sharply-defined limits of pressure. In this region explosion occurs, the passage from slow reaction to explosion being abrupt.

Ultra-violet light of wave-length 2500–2800 Å. diminishes the lower pressure limit.

This effect is shown to be due to the production from the phosphine of a minute amount of an active substance, which does not decay immediately when the illumination ceases. This substance increases the explosibility of the mixture by an action comparable with that exerted by nitrogen peroxide on mixtures of hydrogen and oxygen. The conditions of formation and decay of the active substance are investigated qualitatively and as far as possible quantitatively. The maximum concentration in the photostationary state is deduced, and the efficiency of collisions with the vessel wall in destroying

it is calculated. The oxidation provides an example of a chain reaction in which the existence of definite "material" chains rather than "energy" chains can be experimentally detected.

This investigation was planned in discussions with Dr. R. H. Dalton, during his tenure of a Ramsay Fellowship in Oxford in 1929. He was not able to remain to carry out the experiments, but he is largely responsible for their inception.

Perturbation Problems in Quantum Mechanics.

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1. *Introduction.*

One of the great achievements of the Schrödinger wave-mechanics is the elegance of its perturbation theory, which has brought many problems, formerly considered intractable, within the range of a highly-developed mathematical technique. It is not necessary at this stage to review the numerous applications which have been made of this perturbation theory or to dwell upon its many advantages. The important advance towards an understanding of chemical forces which it has made possible is in itself a considerable achievement.

There are, however, certain disadvantages in the perturbation theory in its present form, which limit the extent of its applications to complex problems of atomic and molecular structure. If the interaction of atoms, for instance, is to be calculated, as is most desirable, improved methods will have to be found.

One such improvement is considered in this paper. In its present form, it is easy to calculate the first approximation of the energy of a system, subject to small perturbations, but difficult to proceed further. This is a considerable disadvantage in those problems where the first approximation vanishes as in calculating the Stark effect or the van der Waals attraction of two atoms at large distances apart. Moreover, the theory expresses the perturbed eigenfunction in terms of all the unperturbed eigenfunctions of

the system and these are not always known. This paper shows how, by a slight modification of the usual method, these difficulties may be overcome and the energy and eigenfunction of a perturbed system calculated to higher approximations with comparative ease.

As an illustration the method is applied to calculate the van der Waals fields of two hydrogen atoms at large distances, and this is done with more ease and directness than the usual form of the theory permits. It is possible, too, to extend the theory to calculate the van der Waals fields of more complicated atoms, as it is hoped to show in a later paper.

The results of the Schrödinger perturbation theory are also obtained by another method, which has the advantage of exhibiting exactly what is neglected in the usual successive approximations. This alternative method is not limited to small perturbations; in fact, it is shown that certain perturbation problems can be solved, however strong the perturbation. One such problem is that of rotating polar molecules under the influence of an external electric field, which is a necessary step in the theory of gaseous dielectrics. A solution of this problem is given and the range of validity of the usual dielectric theory is thus determined.

2. The Usual Perturbation Theory.

(i) *Non-degenerate Cases.*—The usual form in which the perturbation theory is given is somewhat as follows.* Let the wave-equation of an unperturbed system be of the form

$$L(\psi) + Ep\psi = 0, \quad (1)$$

where L denotes a partial linear differential expression of the second order, which is self-adjoint, and p is a factor introduced in the process of making the equation self-adjoint, or indeed any convenient factor, provided that it is continuous in the variables, never becomes negative and also in general does not vanish. We suppose the solutions of equation (1) to be known and that they are orthogonal and normalised as usual, so that

$$\int \psi_i \psi_k p dq = \delta_{ik}, \quad (2)$$

the single variable q being used to denote the whole set of independent variables. The corresponding energy values are also supposed known. We denote them by E_k , ..., and suppose for the present that there is no degeneracy—that is, there is only one eigenfunction ψ_k to every eigenvalue E_k .

* Cf. Sommerfeld, 'Atombau und Spektrallinien, Ergänzungsband,' p. 170 (1929).

The perturbation is represented by the introduction of a term $\lambda(v p \psi)$ on the right-hand side of equation (1), where λ is a parameter, introduced to indicate that the perturbation is supposed small and v is a function of the independent co-ordinates q .

The modified equation is then

$$L(\psi) + (E - \lambda v) p\psi = 0. \quad (3)$$

For every solution of equation (1) there is assumed to be a solution of equation (3) of the type

$$\psi = \psi_k + \lambda \phi_k + \lambda^2 \chi_k + \dots, \quad E = E_k + \lambda \epsilon_k + \lambda^2 \eta_k + \dots \quad (4)$$

Introducing these expressions into equation (3), equating like powers of λ , an equation is found for ϕ_k of the type

$$L(\phi_k) + E_k p\phi_k = (v - \epsilon_k) p\psi_k, \quad (5)$$

and as the inhomogeneous part of the equation, viz., the right-hand side, must be orthogonal to a solution of the homogeneous part, viz., the left-hand side, we infer

$$\epsilon_k = \frac{\int v \psi_k \phi_k p dq}{\int \psi_k^2 p dq}, \quad (6)$$

$$= \frac{\int v \psi_k^2 p dq}{\int \psi_k^2 p dq}, \quad (7)$$

assuming the ψ 's to be real. The formula is easily generalised if they are not.

The appropriate value of ϕ_k is then found by assuming it expanded in terms of the set of functions ψ_i , viz.,

$$\phi_k = \sum_i B_{ki} \psi_i, \quad (8)$$

and then substituting in equation (5), whence it is found that

$$\phi_k = \sum_i' A_{ki} \psi_i / (E_k - E_i), \quad (9)$$

where

$$A_{ki} = \int (v - \epsilon_k) \psi_k \psi_i p dq = \int v \psi_k \psi_i p dq, \quad (10)$$

and the summation extends over all values of i except $i = k$, and includes the continuous spectrum, if such exists.

The second approximation, viz., η_k and χ_k , is obtained from the equation

$$L(\chi_k) + E_k p\chi_k = (v - \epsilon_k) p\phi_k - \eta_k p\psi_k, \quad (11)$$

whence, by the same method as before,

$$\eta_k = \int (v - \varepsilon_k) p \phi_k \psi_k dq, \quad (12A)$$

$$= \sum_i A_{ki} A_{ik} / (E_k - E_i). \quad (12B)$$

It can be shown further that

$$\chi_k = \sum_i (\varepsilon_i - \varepsilon_k) A_{ki} \psi_i / (E_k - E_i)^2. \quad (13)$$

(ii) *Degenerate Cases.*—In the case of degeneracy the procedure is somewhat different in the earlier stages, though it is the same in principle. Suppose that there are α independent solutions, all having the same eigenwert E_k , viz.,

$$\psi_{k1}, \psi_{k2}, \dots, \psi_{ki}, \dots, \psi_{k\alpha}.$$

We suppose that they are normalised and orthogonal not only to all other eigenfunctions but also to each other. It is easy to show that these same properties are retained by any linear orthogonal transformation of the set ψ_{ki} , for example, by

$$\psi_{kh} = \sum_i \beta_{hi} \psi_{ki}, \quad (14)$$

where the α^2 coefficients β_{hi} satisfy the relations

$$\sum_i \beta_{hi} \beta_{h'i} = \delta_{hh'}. \quad (15)$$

Assuming slight perturbations of the functions ψ_{kh} and of E_k owing to the term $\lambda v p \psi$ in equation (3), the same method as before leads to the set of equations

$$\sum \beta_{hi} (v_{ij} - \delta_{ij} \varepsilon) = 0, \quad (i, j = 1, 2, \dots, \alpha), \quad (16)$$

where

$$v_{ij} = \int v \psi_{ki} \psi_{kj} p dq. \quad (17)$$

This set of equations determines the change of energy ε due to the perturbation and the appropriate coefficients β_{hi} . The equation for ε is the determinant

$$|v_{ij} - \delta_{ij} \varepsilon| = 0, \quad (i, j = 1, 2, \dots, \alpha) \quad (18)$$

which has in general α different roots. To any such root ε_h belong a unique set of β 's, say, β_{hi} , ($i = 1, \dots, \alpha$), and so a unique function ψ_{kh} as defined in (14). The perturbation thus in general removes the degeneracy, as it causes a splitting-up of the eigenwert E_k into α separate ones, viz., $E_k + \varepsilon_h$, ($h = 1, \dots, \alpha$), and determines a unique set of functions ψ_{kh} ($h = 1, 2, \dots, \alpha$).

After this preliminary determination of the appropriate ψ_{kh} 's, the method

proceeds as before. It is assumed that the perturbation causes a slight change in the eigenfunctions

$$\psi = \psi_{kh} + \lambda \phi_{kh},$$

and it is found that

$$\phi_{kh} = \sum_l' \sum_i A_{li} \psi_{li} / (E_k - E_l), \quad (19)$$

where

$$A_{li} = \int v \psi_{kh} \psi_{li} p \, dq, \quad (20)$$

and ψ_{li} is any eigenfunction not belonging to the set ψ_{kh} , and is assumed for generality to be the i^{th} member of that set, which before perturbation had the eigenwert E_l .

The second approximation to the energy and eigenfunction can be determined as in the undegenerate case.

3. *A Modified Form of the Usual Perturbation Theory.*

While the method just outlined determines the first approximation to the perturbed energy with great ease and directness, it leaves the perturbed eigenfunction expressed in terms of all the eigenfunctions except that which is perturbed. Now there are many problems where these are not known with any accuracy, though the unperturbed one may already have been found. The perturbation of the helium atom or the hydrogen molecule from its normal state provides a simple example. Moreover, there are many problems in which the first approximation, given by equation (7), vanishes, and the determination of the second approximation can then only be carried out when the whole set of eigenfunctions is known.

By a slight modification of equation (9), viz.,

$$\phi_k = (v - \epsilon_k) \psi_k / E_k + \sum_l' E_l A_{kl} \psi_l / E_k (E_k - E_l) \quad (21)$$

the main part of ϕ_k is expressed in terms of the unperturbed eigenfunction ψ_k , and the rest of the expression is much more convergent than the usual expression (9), particularly when, as often in the normal state, $E_k \gg E_l$. This modification, though almost trivial, greatly extends the scope of the theory, for the next approximation to the energy can be obtained with much greater ease. Thus we get on substituting (21) in equation (12A)

$$\begin{aligned} \eta_k &= \int (v - \epsilon_k)^2 \psi_k^2 p \, dq / E_k + \sum_l' E_l A_{kl} A_{lk} / E_k (E_k - E_l), \\ &= \int v^2 \psi_k^2 p \, dq / E_k - \epsilon_k^2 / E_k + \sum_l' E_l A_{kl} A_{lk} / E_k (E_k - E_l). \end{aligned} \quad (22)$$

The first integral is as easy to evaluate as ϵ_k and the remaining summation usually converges rapidly.

In the same way, it can be shown that the expression for χ_k , the next term to be added to ψ_k in the process of approximation, given above in (13), may be transformed to

$$\chi_k = \left\{ \frac{(v - \epsilon_k)^2}{E_k} - \eta_k \right\} \frac{\psi_k}{E_k} + \frac{(v - \epsilon_k)}{E_k} \sum_i' \frac{E_i A_{ki} \psi_i}{E_k (E_k - E_i)} + \sum_i' \frac{E_i (\epsilon_i - \epsilon_k) A_{ki} \psi_i}{E_k (E_k - E_i)^2}, \quad (23)$$

the main part of which again involves only ψ_k and known quantities.

The solution of the equation

$$L(\psi) + (E - v)p\psi = 0, \quad (24)$$

putting $\lambda = 1$ in (3), is thus to the second approximation

$$\begin{aligned} \Psi_k &= \psi_k + \phi_k + \chi_k \\ &= \psi_k \left\{ \left(1 - \frac{\epsilon_k + \eta_k}{E_k} + \frac{\epsilon_k^2}{E_k^2} \right) + v \left(\frac{1}{E_k} - \frac{2\epsilon_k}{E_k^2} \right) + \frac{v_k^2}{E_k^2} \right\} \\ &\quad + \sum_i' \left\{ 1 + \frac{v - \epsilon_k}{E_k} + \frac{\epsilon_i - \epsilon_k}{E_k - E_i} \right\} \frac{E_i A_{ki} \psi_i}{E_k (E_k - E_i)}. \end{aligned} \quad (25)$$

It appears, therefore, that in difficult problems which can only be solved by variation methods, a suitable substitution for the eigenfunction is

$$\Psi_k = \{a + bv + cv^2 + \dots\} \psi_k, \quad (26)$$

where $a, b, c, \dots$ are parameters to be evaluated by the usual variational method. Prof. H. R. Hassé, of this University, has in fact found empirically that the simple substitution $(a + bv)\psi_k$ is an effective one in certain variation problems, an account of which is to be published shortly.*

Degenerate problems may be treated in a similar way. In the notation of the preceding paragraph the appropriate set of functions ψ_{kh} ($h = 1, 2, \dots, \alpha$) belonging to the same E_k are determined as before by equation (16). Instead of writing as in (19),

$$\phi_{kh} = \sum_i' \sum_l A_{li} \psi_{li} / (E_k - E_l), \quad (27)$$

we use the fact that

$$(v - \epsilon_{kh}) \psi_{kh} = \sum_i' \sum_l A_{li} \psi_{li}, \quad (28)$$

and then find

$$\phi_{kh} = (v - \epsilon_{kh}) \psi_{kh} / E_k + \sum_i' \sum_l E_l A_{li} \psi_{li} / E_k (E_k - E_l). \quad (29)$$

* 'Proc. Camb. Phil. Soc.,' Oct. 1930.

As the summation omits the value $l = k$, the first term may be the most important, especially if $E_l \ll E_k$ for all l .

The equation to determine the next approximation χ_{kh} is found by the Schrödinger method to be

$$L(\chi_{kh}) + E_k p \chi_{kh} = (v - \epsilon_{kh}) p \phi_{kh} - \eta_{kh} p \psi_{kh}, \quad (30)$$

and the condition that the right-hand side shall be orthogonal to all the solutions of the left leads to

$$\eta_{kh} = \int (v - \epsilon_{kh}) \phi_{kh} \psi_{kh} p \, dq, \quad (31)$$

and using the expression (29) just obtained for ϕ_{kh} , this becomes

$$\eta_{kh} = \frac{1}{E_k} \int v^2 \psi_{kh} \psi_{kh} p \, dq - \frac{\epsilon_{kh}^2}{E_k} + \sum' \sum \frac{E_l A_{lh}^{kh} A_{kh}^{lh}}{E_k (E_k - E_l)}, \quad (32)$$

where

$$A_{lh}^{kh} = \int v \psi_{kh} \psi_{lh} p \, dq, \quad (33)$$

and the summation excludes the case $l = k$.

4. A More General Perturbation Theory.

The results of the Schrödinger perturbation theory can be obtained in a rather different way, which has the advantage of indicating exactly what is neglected in the usual method and of dispensing with the assumption that the perturbation is small. The problem is to find a solution of the equation

$$L(\psi) + (E - v) p \psi = 0, \quad (34)$$

when that of equation (1), viz.,

$$L(\psi) + E p \psi = 0,$$

is known.

Assume that the solution of (34) can be expressed in terms of the set of functions, which are solutions of (1), viz.,

$$\psi = \sum_i a_i \psi_i. \quad (35)$$

We have further

$$v \psi_i = \sum_j v_{ij} \psi_j, \quad (36)$$

where

$$v_{ij} = \int v \psi_i \psi_j p \, dq, \quad (37)$$

or

$$v_{ij} = \int v \psi_i \psi_j^* p \, dq, \quad (38)$$

if the eigenfunctions are not real. It is easy to carry out this generalisation, but for simplicity we will suppose the ψ 's to be real.

Then

$$v\psi = \sum_i v a_i \psi_i = \sum_i a_i v \psi_i = \sum_i a_i \sum_j v_{ij} \psi_j. \quad (39)$$

Substituting in equation (34) for ψ and $vp\psi$, we find

$$\sum_i a_i (E - E_i) p \psi_i = \sum_i a_i \sum_j v_{ij} p \psi_j, \quad (40)$$

and equating coefficients of like ψ_i 's, we then get

$$a_i (E - E_i) = \sum_j a_j v_{ji}, \quad (j = 1, 2, \dots) \quad (41)$$

which is a system of equations to determine the a 's and the possible values of E . Thus eliminating the a 's, we obtain the determinant

$$\begin{vmatrix} v_{11} - \overline{E - E_1}, & v_{12} & & & \\ v_{21} & & v_{22} - \overline{E - E_2}, & & \\ . & . & . & . & . \\ . & . & . & . & . \end{vmatrix} = 0. \quad (42)$$

The values of $E_1, E_2, \dots$ are supposed known, and v_{ij} can be evaluated by quadrature. We thus have a determinant which may have an infinite number of rows and columns.

The successive approximations of the Schrödinger method may be obtained as follows : First, to be definite, suppose that it is the perturbation of E_1 which is required. Neglect every v_{ij} except v_{11} and we get the first approximation

$$E = E_1 + v_{11} = E_1 + \int v \psi_1^2 p dq. \quad (43)$$

Next, neglect every v_{ij} except those in the first row and column. Then we get the bordered determinant

$$\begin{vmatrix} v_{11} - \overline{E - E_1}, & v_{12} & v_{13} & . & . & . \\ v_{21} & & \overline{E_2 - E}, & 0 & . & . \\ v_{31} & & 0 & \overline{E_3 - E}, & . & . \\ . & . & . & . & . & . \end{vmatrix} = 0. \quad (44)$$

By an elementary theorem of determinants, the expansion of this is

$$(v_{11} - \overline{E - E_1}) \pi_2 - \sum_j' v_{1j} v_{j1} \pi_2 / (E_j - E) = 0,$$

where the summation includes all values of j except $j = 1$, and

$$\pi_2 = (E_2 - E)(E_3 - E) \dots$$

Hence the equation to determine E is

$$E - E_1 = v_{11} + \sum_j' v_{1j} v_{j1} / (E - E_j), \quad (45)$$

which is identical with the sum of ϵ_k and η_k obtained in equations (7) and (12b), putting $k = 1$ and allowing for the differences of notations, except that E now appears in each denominator of the summations on the right-hand side. As a first approximation we may put $E = E_1$ on the right-hand side, and then as a second put $E = E_1 + v_{11}$ on the right and find the new value of E on the left. The process can then be continued until E is found to any required degree of accuracy.

Of course, for more accurate solutions other elements v_{ij} must be introduced into the determinant. If the second row and column are introduced as well as the first, it is still possible to expand the determinant without difficulty by considering first the inner bordered determinant and then considering the complete determinant as a border of that.

The greater the perturbation, the greater the number of elements which must be retained in the determinant, but theoretically the method is applicable however large the perturbation.

When there is degeneracy before perturbation, the preliminary step is the same as that of the usual method, outlined in the preceding paragraph, that is, a set of eigenfunctions ψ_{kh} ($h = 1, 2, \dots \alpha$) are determined by equation (16), viz.,

$$\sum_i \beta_{hi} (v_{ij} - \delta_{ij} \epsilon) = 0, \quad (i, j = 1, 2, \dots \alpha) \quad (46)$$

With the set of ψ_{kh} so determined, the determinantal equation becomes a diagonal one.

The general determinantal equation (42) now takes the form shown below. The shaded areas represent further diagonal arrays, all the elements within the area vanishing except those on the diagonal.

$$\begin{vmatrix}
 v_{k1}^{(k1)} - \overline{E} - E_k & 0 & \dots & 0 & v_{i1}^{(k1)}, v_{i2}^{(k1)}, & \dots & \dots & \dots \\
 0 & v_{k2}^{(k2)} - \overline{E} - E_k & \dots & 0 & v_{i1}^{(k2)}, v_{i2}^{(k2)}, & \dots & \dots & \dots \\
 \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\
 \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\
 0 & 0 & \dots & v_{ka}^{(ka)} - \overline{E} - E_k & v_{i1}^{(ka)}, v_{i2}^{(ka)}, & \dots & \dots & \dots \\
 \hline
 v_{k1}^{(i1)}, & v_{k2}^{(i1)}, & \dots & v_{ka}^{(i1)} & \text{shaded square} & \dots & \dots & \dots \\
 v_{k1}^{(i2)}, & v_{k2}^{(i2)}, & \dots & v_{ka}^{(i2)} & \text{shaded square} & \dots & \dots & \dots \\
 \dots & \dots & \dots & \dots & \dots & \text{shaded square} & \dots & \dots \\
 \dots & \dots & \dots & \dots & \dots & \dots & \text{shaded square} & \dots \\
 \dots & \dots & \dots & \dots & \dots & \dots & \dots & \text{shaded square}
 \end{vmatrix} = 0. \quad (47)$$

In general, no elements vanish outside the chain of squares along the diagonal.

The first approximation of the Schrödinger method is obtained by neglecting every v_{ij} except those contained within the shaded squares. Thus we get

$$\begin{aligned}
 E &= E_k + v_{kh}^{kh} = E_k + \int v \psi_{kh}^{kh} \psi_{kh}^{kh} p \, dq \\
 &= E_k + \epsilon_{kh}. \quad (h = 1, 2, \dots, \alpha) \quad (48)
 \end{aligned}$$

The second approximation is obtained by omitting every v_{ij} except those within the squares and one row and column which cross on the diagonal. By transpositions of the determinant till this row and column occupy positions at the top and side of the determinant, it becomes a bordered determinant of the ordinary type and the expression

$$E = E_k + v_{kh}^{kh} + \sum_i' \sum_j v_{kh}^i v_{ik}^{jh} / (E - E_i) \quad (49)$$

is obtained.

To transform this expression and the corresponding one (45) into the more practical form given in the preceding paragraph, all we need do is to use the fact that

$$(v^2)_{kh}^{kh} = \sum_i' \sum_j v_{kh}^i v_{ik}^{jh}$$

from matrix algebra. We then get

$$E = E_k + v_{kk}^{kh} + (v_{kh}^{kh})^2/E + \sum_i' \sum_l E_l v_{kl}^{kl} v_{li}^{kl}/E (E - E_l). \quad (50)$$

When the energy values have thus been determined by any suitable numerical method, the corresponding eigenfunctions which were assumed to be $\psi = \sum_i a_i \psi_i$ are given by the set of equations (41) or by a determinant of the type

$$\Psi = \begin{vmatrix} \psi_1 & \psi_2 & & & \psi_i & & & \\ v_{21} & v_{22} - \overline{E - E_2} & & & v_{2i} & & & \\ & & & & & & & \\ & & & & & & & \\ v_{i1} & v_{i2} & & & v_{ii} - \overline{E - E_i} & & & \\ & & & & & & & \end{vmatrix} \quad (51)$$

where the values of E already found are substituted.

By neglecting every element v_{ij} except those in the first column, an expression similar to that of equation (25) can be obtained. Further approximations can be found by taking into account, for example, each v_{ii} on the diagonal and then the second column, and so on. In particular cases, some of the v_{ij} 's vanish and then the determinant can be evaluated by special methods. An example is given in § 6 below.

5. The Interaction of Two Hydrogen Atoms at Large Distances.

The results of the preceding paragraphs may be applied to a number of problems, but it is instructive to apply the methods of this paper to a problem which has already been considered by the usual methods. A problem recently considered is that of the interaction of two hydrogen atoms at a large distance.* Eisenschitz and London carry out the Heitler and London† calculations to a second approximation, but find that these can only be carried out numerically when the distance between the atoms is large. For large distances the usual 'austausch' effect can be neglected and the unperturbed eigenfunction written simply as a product of the separate hydrogen eigenfunctions, viz.,

$$u_1 = \psi_1(1) \phi_1(2).$$

* Eisenschitz and London, 'Z. Physik,' vol. 60, p. 491 (1930).

† Heitler and London, 'Z. Physik,' vol. 44, p. 445 (1927).

If the two electrons are denoted by 1 and 2, and the distances from one nucleus by r and those from the other by p , the perturbation term is

$$v = -e^2 \left(\frac{1}{p_1} + \frac{1}{r_2} - \frac{1}{r_{12}} - \frac{1}{R} \right), \quad (52)$$

where r_{12} is the distance between the electrons and R that between the nuclei. Now if R is large and the electrons are assumed never to be very far from their respective nuclei, so that r_1 and p_2 are small, we can write

$$v = \frac{e^2 r_1 p_2}{R^3} \{ \cos(\mathbf{r}_1, \mathbf{p}_2) - 3 \cos(\mathbf{r}_1, \mathbf{R}) \cos(\mathbf{p}_2, \mathbf{R}) \} + \frac{1}{R^4} \{ \dots \} + \dots \quad (53)$$

Neglecting all except the first term in v , as only the asymptotic form of the interaction is required, it is easy to see that the first approximation to the perturbed energy vanishes. We have

$$\epsilon = v_{11} = \int v \psi_1^2(1) \phi_1^2(2) p \, dr_1 \, dr_2 = 0,$$

where the integration is taken over the whole of space for electrons 1 and 2 separately, and here $p = 1$.

The second one is written

$$\eta = \sum_k' v_{1k} v_{k1} / (E_1 - E_k),$$

where

$$v_{1k} = \int v \psi_1(1) \psi_k(1) \phi_1(2) \phi_k(2) \, d\tau_1 \, d\tau_2,$$

and after some reduction it is found that

$$\eta = - \frac{e^2}{a_0(R/a_0)^6} 12 \sum_{n'n''}' \frac{f_{1n'} f_{1n''}}{(1 - 1/n'^2)(1 - 1/n''^2)(2 - 1/n'^2 - 1/n''^2)}, \quad (54)$$

where the f 's are the same as appear in the usual dispersion formula, and a_0 is the atomic unit of length. The summation extends over all integral values of n' and n'' independently and includes the continuous part of the spectrum as well. The f 's have previously been worked out by Sugiura* and are given by

$$f_{1n} = \frac{2^8}{3} \frac{n^5 (n-1)^{2n-4}}{(n+1)^{2n+4}}. \quad (55)$$

For the continuous region London and Eisenschitz use the formula

$$\frac{df_{1E}}{dE} = \frac{2^7}{3} \frac{e^{-4} (1 + 4E/3)}{(1 + E)^4}, \quad (56)$$

* Sugiura, 'J. Phys.', vol. 8, p. 113 (1927).

and show that it is a good approximation to the correct formula given by Sugiura.*

It is then found that the summation leads to the following values

$$\sum_{n'n''} = 0.329, \quad \sum_{n'} \int dE'' + \sum_{n''} \int dE' = 0.184, \quad \iint dE' dE'' = 0.027, \quad (57)$$

so that

$$\eta = - \frac{e^2}{a_0 (R/a_0)^6} 12 (0.540) = - \frac{175}{(R/a_0)^6} \text{ volts.} \quad (58)$$

By the method of § 3, however, we get, using formula (22), and putting $p dq = d\tau_1 d\tau_2$

$$\begin{aligned} \eta = & - \frac{1}{2|E_0|} \int v^2 \psi_1^2(1) \phi_1^2(2) d\tau_1 d\tau_2 \\ & - \frac{e^2}{a_0 (R/a_0)^6} 12 \sum'_{n'n''} \frac{f_{1n'} f_{1n''} (1/n'^2 + 1/n''^2)}{2(1 - 1/n'^2)(1 - 1/n''^2)(2 - 1/n'^2 - 1/n''^2)}, \end{aligned} \quad (59)$$

where the second summation extends over all integral values of n' and n'' , except $n' = n'' = 1$, and the continuous region of both atoms, just as the summation which occurs in the expression of Eisenschitz and London, given above in equation (54); in fact, the summation given here differs from theirs only in the introduction of a factor $\frac{1}{2}(1/n'^2 + 1/n''^2)$. This factor, however, considerably improves the convergence and permits of easier calculation.

The first term in equation (59) is easily calculated, using the expression (53) for v . We have

$$\begin{aligned} & \int \phi_1(2) p_2^2 \{ \cos(\mathbf{r}_1, \mathbf{p}_2) - 3 \cos(\mathbf{r}_1, \mathbf{R}) \cos(\mathbf{p}_2, \mathbf{R}) \}^2 d\tau_2 \\ & = \{1 + 3 \cos^2(\mathbf{r}_1, \mathbf{R})\} \int \phi_1^2(2) p_2^2 \cos^2(\mathbf{p}_2, \mathbf{R}) d\tau_2 \\ & = \{1 + 3 \cos^2(\mathbf{r}_1, \mathbf{R})\} a_0^3, \end{aligned} \quad (60)$$

if we substitute for $\phi_1(2)$ the eigenfunction for the normal state. Hence

$$\begin{aligned} \eta = & - \frac{e^4}{2|E_0| R^6} \int \psi_1^2(1) r_1^2 \{1 + 3 \cos^2(\mathbf{r}_1, \mathbf{R})\} a_0^3 d\tau_1 - \frac{e^2}{a_0 (R/a_0)^6} 12 \sum'_{n'n''} \\ & = - \frac{e^4}{2|E_0| R^6} \cdot 6a_0^4 - \frac{e^2}{a_0 (R/a_0)^6} 12 \sum'_{n'n''} \\ & = - \frac{e^2}{a_0 (R/a_0)^6} 12 \left\{ 0.5 + \sum'_{n'n''} \right\}, \end{aligned} \quad (61)$$

* Sugiura, *loc. cit.*

since $|E_0|$ is the energy of the normal state of the hydrogen atom and is equal to $e^2/2a_0$.

The first term of the summation $\sum_{n'n''}$ is equal to 0.051, and all the rest (including (i) the discontinuous range of n' with that of n'' , (ii) the continuous range of one with the discontinuous range of the other, (iii) the continuous range of both) only yields -0.011 .

We thus get

$$\eta = -\frac{e^2}{a_0(R/a_0)^6} 12(0.540) = -\frac{175}{(R/a_0)^6} \text{ volts,}$$

as do Eisenschitz and London, but the ease of calculation is to be compared with that involved in equation (57). The latter involve series of slow convergence, which can only be evaluated with great labour. The results are summarised in the following table:—

Eisenschitz and London.		New method.	
$\sum_{n'n''}$	Discontinuous-Discontinuous	Integral	0.500
	Discontinuous-Continuous	New $\sum'$ First term	0.051
	Continuous-Discontinuous	$\sum''$ Rest	-0.011
	Continuous-Continuous		
	0.540		0.540

6. The Dielectric Theory of a Polar Gas.

To illustrate the advantage of using the determinantal method, given in § 4, we consider the perturbation of rotating polar molecules in an electric field, a problem occurring in the theory of dielectrics.*

The wave-equation for rotating molecules, which are symmetrical about an axis, is

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 A}{h^2} E \psi = 0, \quad (62)$$

where θ and ϕ are the usual angular co-ordinates of the molecular axis, A is the moment of inertia and E the energy. The values of E are given by

$$E = \frac{h^2}{8\pi^2 A} l(l+1), \quad (63)$$

* Cf. Debye, 'Polare Molekeln,' Leipzig, chap. 9, 1929.

and the normalised eigenfunctions by*

$$\psi_{l,m} = P_l^m(\cos \theta) e^{im\phi} / N_\theta \cdot N_\phi, \quad (64)$$

where

$$N_\phi = \sqrt{2\pi}, \quad N_\theta = \left(\frac{2}{2l+1} \right)^{\frac{1}{2}} \left\{ \frac{(l+m)!}{(l-m)!} \right\}^{\frac{1}{2}}, \quad (65)$$

and $P_l(\cos \theta)$ is the usual Legendre function, while

$$P_l^m(\cos \theta) = \sin^m \theta \frac{dP_l(\cos \theta)}{d(\cos \theta)^m}. \quad (66)$$

To find the perturbed energy levels, when the molecules are subject to an electric field, we introduce in equation (62) a perturbing potential $-\mu F \cos \theta$, where μ is the permanent electric moment of the molecule and F the applied electric field. The equation then reads

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \{\lambda + \kappa \cos \theta\} \psi = 0, \quad (67)$$

where

$$\kappa = \mu F \frac{8\pi^2 A}{h^2}, \quad \lambda = E \frac{8\pi^2 A}{h^2}. \quad (68)$$

In the notation of § 4,

$$v = \kappa \cos \theta, \quad (69)$$

and expanding $v\psi_{l,m}$ as in equation (36), we find

$$v\psi_l = \kappa \cos \theta \psi_{l,m} = v_{l,l-1}^{(m)} \psi_{l-1,m} + v_{l,l+1}^{(m)} \psi_{l+1,m}, \quad (70)$$

where

$$v_{l,l-1}^{(m)} = v_{l-1,l}^{(m)} = \frac{(l+m)! (l-m)!}{(2l-1)! (2l+1)!} \kappa. \quad (71)$$

Every other $v_{l,l'}^{(m)}$ vanishes.

It is to be noted that in the expansion no eigenfunction on the right appears which contains a factor $e^{im'\phi}$, where $m' \neq m$. The determinant in the determinantal equation, therefore, splits up into a product of determinants, so that each term of each determinant contains the same m . A typical such determinant is

$$\begin{vmatrix} \lambda_m - \lambda, & v_{m+1,m}^{(m)}, & 0, & \dots \\ v_{m,m+1}^{(m)}, & \lambda_{m+1} - \lambda, & v_{m+2,m+1}^{(m)}, & \dots \\ 0, & v_{m+1,m+2}^{(m)}, & \lambda_{m+2} - \lambda, & \dots \\ \cdot & \cdot & \cdot & \dots \\ \cdot & \cdot & \cdot & \dots \end{vmatrix} = 0. \quad (72)$$

* Sommerfeld, 'Atombau und Spektrallinien,' Ergänzungsband, pp. 62 and 64 (1929).

If the perturbation is small, so that κ is small, the approximate solution for that root of the equation which lies in the neighbourhood of E_l can be obtained from the equation

$$\begin{vmatrix} \lambda_{l-1} - \lambda, & v_{l,l-1}, & 0 \\ v_{l-1,l}, & \lambda_l - \lambda, & v_{l+1,l} \\ 0, & v_{l,l+1}, & \lambda_{l+1} - \lambda \end{vmatrix} = 0, \quad (73)$$

which leads to

$$\lambda_l - \lambda = v_{l,l-1}^2 / (\lambda_{l-1} - \lambda) + v_{l+1,l}^2 / (\lambda_{l+1} - \lambda).$$

If λ is put equal to $l(l+1)$ on the right-hand side, we find

$$E = E_l - (\hbar^2/8\pi^2A) [\Phi_{l+1}^{(m)} - \Phi_l^{(m)}] \kappa^2/2, \quad (74)$$

where

$$\Phi_l^{(m)} = \frac{(l-m)(l+m)}{l(2l-1)(2l+1)}. \quad (75)$$

In particular, the perturbation of the lowest energy level ($l=0, m=0$) is

$$E = -(\hbar^2/8\pi^2A) (\kappa^2/6). \quad (76)$$

These results are the same as those generally used in the theory of dielectrics.*

In the case of large electric fields, when κ can no longer be assumed small, the whole of the determinant (72) must be considered. The perturbation of the lowest level ($l=0, m=0$) is then given by

$$\begin{vmatrix} -\lambda, & \kappa/3^{\frac{1}{2}}, & 0, & \dots \\ \kappa/3^{\frac{1}{2}}, & \lambda_1 - \lambda, & 2\kappa/3^{\frac{1}{2}}5^{\frac{1}{2}}, & \dots \\ 0, & 2\kappa/3^{\frac{1}{2}}5^{\frac{1}{2}}, & \lambda_2 - \lambda, & \dots \\ \cdot & \cdot & \cdot & \dots \\ \cdot & \cdot & \cdot & \dots \end{vmatrix} = 0, \quad (77)$$

which is equivalent to

$$\lambda \Delta_1 + (\kappa^2/3) \Delta_2 = 0,$$

where Δ_1 is the determinant obtained from the above by omitting the first row and column, Δ_2 that obtained by omitting the first two rows and columns.

Hence

$$\lambda = -(\Delta_2/\Delta_1) (\kappa^2/3).$$

* Debye, *loc. cit.*, where earlier references are given.

Again, expanding Δ_1 we have

$$\Delta_1 = (\lambda_1 - \lambda) \Delta_2 - (2 \cdot 2 \kappa^2 / 3 \cdot 5) \Delta_3,$$

so that

$$\frac{\Delta_2}{\Delta_1} = \frac{1}{(\lambda_1 - \lambda) - \frac{2 \cdot 2 \cdot \kappa^2}{3 \cdot 5} \frac{\Delta_3}{\Delta_2}}.$$

The process can be continued, with the result that

$$\begin{aligned} \lambda &= - \frac{\kappa^2/3}{(\lambda_1 - \lambda) - \frac{2^2 \kappa^2/3 \cdot 5}{(\lambda_2 - \lambda) - \frac{3^2 \kappa^2/5 \cdot 7}{(\lambda_3 - \lambda) - \dots}}} \\ &= - \frac{\kappa^2/3}{(1 \cdot 2 - \lambda) - \frac{2^2 \kappa^2/3 \cdot 5}{(2 \cdot 3 - \lambda) - \frac{3^2 \kappa^2/5 \cdot 7}{(3 \cdot 4 - \lambda) - \dots}}} \end{aligned} \quad (78)$$

and

$$E = \lambda (\hbar^2/8\pi^2 A).$$

The result (78) is true for all values of κ , large or small, and λ can be evaluated with comparative ease when κ is known. Thus if $\kappa = 1$, we find for the perturbation of the normal state $\lambda = -0.158$. The usual approximation, which is $\lambda = -\kappa^2/6$, gives -0.167 , a result which is about 6 per cent. too large. Now

$$\kappa = 8\pi^2 A \mu F / \hbar^2, \quad (79)$$

and a typical value of μ is 10^{-18} electrostatic units, and A , the moment of inertia, may have a value varying from 10^{-40} to 10^{-37} (HCl has a value of A equal to $2.65 \cdot 10^{-40}$ and I_2 a value of $742.6 \cdot 10^{-40}$). In the case of the iodine molecule, where $\mu = 1.2 \cdot 10^{-18}$ and $A = 742.6 \cdot 10^{-40}$, κ has a value of about unity, when F is of the order of 1300 volts per centimetre. For such fields it is no longer legitimate to use the formula $\lambda = -\kappa^2/6$ for the perturbed energy. For gases with a smaller value of A , the permissible value of F becomes higher. In most experimental methods fields of not more than a hundred volts or so are used, and we infer that for these the usual theory is valid.

When the formula $\lambda = -\kappa^2/6$ is no longer applicable, it is incorrect to use the usual formula†

$$m = \mu^2 F / 3\kappa T \quad (80)$$

* Debye, *loc. cit.*, p. 195.

† Debye, *loc. cit.*, p. 172.

for the mean moment of a polar gas under the influence of a field F . A new formula for m must be worked out from first principles, viz.,

$$m = - \frac{\partial \phi}{\partial F} = \frac{\kappa T}{\sigma} \frac{\partial \sigma}{\partial F}, \quad (81)$$

where σ is the partition function, given by

$$\sigma = \sum_i q_i e^{-E_i(F)/kT}, \quad (82)$$

the summation being taken over all the rotational energy levels of the molecules, considered as functions of the applied field F , and q_i is the weight of the various levels; we have $q_i = 1$, when $m = 0$ and $q_i = 2$ otherwise.

The perturbed eigenfunctions are given by the series of determinants obtained by giving to m all integral values in the following expression and giving to λ the numerical values of the roots of equation (72)

$$\Psi = \begin{vmatrix} \psi_{m,m} & \psi_{m+1,m} & \psi_{m+2,m} & \dots \\ v_{m,m+1}^{(m)} & \lambda_{m+1} - \lambda & v_{m+2,m+1}^{(m)} & \dots \\ 0 & v_{m+1,m+2}^{(m)} & \lambda_{m+2} - \lambda & \dots \\ \cdot & \cdot & \cdot & \dots \\ \cdot & \cdot & \cdot & \dots \end{vmatrix}.$$

7. Summary.

1. A modified form of the Schrödinger perturbation theory is given, which considerably extends its scope and permits of the more accurate determination of perturbed energy values.

2. A more general perturbation theory is given as well, which is not limited to small perturbations.

3. The van der Waals attraction of two hydrogen atoms at large distances apart is evaluated.

4. The dielectric theory of a polar gas is considered for large applied electric fields.

*Theory of the Elastic Scattering of Electrons in
Molecular Hydrogen.*

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Since the introduction of quantum mechanical methods, the theory of scattering of electrons by atoms and ions has been developed very considerably. In the case of elastic collisions it is possible to determine the effective cross sections presented by atoms to a beam of electrons, from a knowledge of the potential in the atom.* This has been done for helium by Mott† and the calculated cross sections agree well with the experimental. Unfortunately, the simplest theoretical case, that of the elastic scattering of electrons by atomic hydrogen, the theory of which has been given by Elsasser,‡ is extremely difficult to attain experimentally, 50 to 60 per cent. atomic hydrogen being the maximum at present attainable. It thus would seem of interest to consider what effects would be expected by using molecular instead of atomic hydrogen. This case is also novel in that we are considering an axially symmetrical field and the number of electrons scattered through a given angle depends on the orientation of the axis relative to the initial and final beams. In an actual case the axes of the molecules may be taken as in random directions, the hydrogen molecule having no permanent dipole moment and so being only slightly oriented by the electric field of the incident beam. This permits us to average the scattering over all orientation to obtain experimental conditions.

§ 1. *General Description of Method.*—It is necessary to restrict the calculation to electron velocities of such magnitude that resonance effects are not of importance and consider elastic collisions. Let ψ_1 be the wave-function representing the state of the scattering system, $\mathbf{n}_0$, $\mathbf{n}_1$ unit vectors in the direction of the initial and final electron motions, m the electron mass, h Planck's constant, v the electron velocity, and $\kappa = 2\pi mv/h$.

Then we find, from Born's collision formula,§ that the scattering cross

* Providing the electron beam is not too slow, when the theory fails.

† 'Proc. Camb. Phil. Soc.', vol. 25, p. 304 (1929).

‡ 'Z. Physik,' vol. 45, p. 522 (1927).

§ 'Z. Physik,' vol. 38, p. 803 (1926).

section for elastic collisions of the system in state I for electrons of velocity v , is

$$\frac{4\pi^2 m^2}{h^4} \left| \int_{-\infty}^{+\infty} V \bar{\psi}_1 \psi_1 e^{i\kappa(\mathbf{a}_1 - \mathbf{a}_0) \cdot \mathbf{r}_1} dv \right|^2, \quad (1)$$

where $\mathbf{r}_1$ is the position vector of the electron and V the inter-action energy.

Let now

r_1, p_1 be the distances of the scattered electron (1) from nuclei 1 and 2 respectively.

r_2, p_2 be the distances of the bound electron (2) from nuclei 1 and 2 respectively.

r_3, p_3 be the distances of the bound electron (3) from nuclei 1 and 2 respectively.

Then we take for ψ_1 , the function obtained by Wang,* using the Ritz method :

$$\psi_1 = C \{ e^{-Z(r_1+p_1)/a_0} + e^{-Z(r_2+p_2)/a_0} \},$$

where a_0 = the radius of the ground orbit of the hydrogen atom and $Z = 1.166$.

For V we have the Coulomb inter-action terms

$$e^2/r_1 + e^2/p_1 - e^2/r_{12} - e^2/r_{13},$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, $r_{13} = |\mathbf{r}_1 - \mathbf{r}_3|$, so we thus are led to consider the integral

$$C^2 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} (e^2/r_1 + e^2/p_1 - e^2/r_{12} - e^2/r_{13}) \{ e^{-Z(r_1+p_1)/a_0} + e^{-Z(r_2+p_2)/a_0} \}^2 \\ \times e^{i\kappa(\mathbf{a}_1 - \mathbf{a}_0) \cdot \mathbf{r}_1} dv_1 dv_2 dv_3. \quad (2)$$

Here C^2 is the normalising factor defined by

$$C^2 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \{ e^{-Z(r_1+p_1)/a_0} + e^{-Z(r_2+p_2)/a_0} \}^2 dv_2 dv_3 = 1, \quad (3)$$

so that

$$C^2 = \{ \pi (a_0/Z)^6 (2 + 2S) \}^{-1},$$

where $S = (1 + \rho + \frac{1}{2}\rho^2) e^{-2\rho}$, $\rho = Zd/a_0$, d being the distance between the nuclei. Owing to the symmetry of the integral (2) in the nuclear co-ordinates, and in the co-ordinates of electrons 2 and 3 it may be written in the form

$$2C^2 (I_1 + I_2 + \sqrt{S} I_3) \pi (a_0/Z)^3,$$

* 'Phys. Rev.', vol. 31, p. 579 (1928).

where

$$I_1 = \iint (e^2/r_1 - e^2/r_{12}) e^{-2Zr_1/a_0} e^{i\kappa(\mathbf{n}_1 - \mathbf{n}_0) \cdot \mathbf{r}} dv_1 dv_2,$$

$$I_2 = \iint (e^2/p_1 - e^2/r_{12}) e^{-2Zp_1/a_0} e^{i\kappa(\mathbf{n}_1 - \mathbf{n}_0) \cdot \mathbf{r}} dv_1 dv_2,$$

$$I_3 = \iint (e^2/r_1 + e^2/p_1 - 2e^2/r_{12}) e^{-Z(r_1 + p_1)/a_0} e^{i\kappa(\mathbf{n}_1 - \mathbf{n}_0) \cdot \mathbf{r}} dv_1 dv_2.$$

Of these the first two are very similar to those occurring in the elastic scattering by atomic hydrogen, while the third represents the effect of the molecular binding.

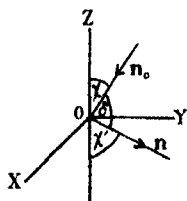


FIG. 1.

§ 2. *Calculation of I_1 and I_2 .*—In these integrals it must be carefully noted that the vector $\mathbf{r}$ refers to an origin at the centre of the molecule, while the distances, r_1 , p_1 , etc., are from the nuclei. Let us choose the nuclear axis as z -axis and the y -axis in the plane of z and $\mathbf{n}_0$, so we may write, in terms of unit vectors $\mathbf{i}, \mathbf{j}, \mathbf{k}$, along the co-

ordinate axes:—

$$\mathbf{n}_0 = \beta\mathbf{j} + \gamma\mathbf{k}, \quad \mathbf{n}_1 = a\mathbf{i} + b\mathbf{j} + c\mathbf{k},$$

$$\mathbf{n}_1 - \mathbf{n}_0 = a\mathbf{i} + (b - \beta)\mathbf{j} + (c - \gamma)\mathbf{k}.$$

If $\mathbf{r}_1, \mathbf{p}_1$, are the position vectors of the electron referred to the two nuclei respectively, d the nuclear separation, we have

$$\mathbf{r} = \frac{1}{2}d\mathbf{k} + \mathbf{p}_1,$$

$$= -\frac{1}{2}d\mathbf{k} + \mathbf{r}_1,$$

so

$$(\mathbf{n}_1 - \mathbf{n}_0) \cdot \mathbf{r} = \frac{1}{2}d(c - \gamma) + (\mathbf{n}_1 - \mathbf{n}_0) \cdot \mathbf{p}_1,$$

$$= -\frac{1}{2}d(c - \gamma) + (\mathbf{n}_1 - \mathbf{n}_0) \cdot \mathbf{r}_1.$$

Taking now δ as the angle of scattering, χ the angle between $\mathbf{n}_0$ and the nuclear axis, χ' between $\mathbf{n}_1$ and the axis, we have the relations

$$\mathbf{n}_1 \cdot \mathbf{n}_0 = \cos \delta = b\beta + c\gamma; \quad \gamma = \cos \chi, \quad \beta = \sin \chi; \quad c = \cos \chi'. \quad (5)$$

Including the equation

$$a^2 + b^2 + c^2 = 1,$$

these suffice to determine a, b, c, β, γ in the above in terms of δ, χ, χ' . Hence

$$I_1 = e^{-\frac{1}{2}i\kappa d(c-\gamma)} I,$$

$$I_2 = e^{\frac{1}{2}i\kappa d(c-\gamma)} I,$$

$$I = \iint (e^2/r_1 - e^2/r_{12}) e^{-2Zr_1/a_0} e^{i\kappa(\mathbf{n}_1 - \mathbf{n}_0) \cdot \mathbf{r}} dv_1 dv_2$$

and so

$$I_1 + I_2 = 2 \cos \{ \kappa d (c - \gamma) \} I, \quad (6)$$

where I is just the integral occurring in the elastic scattering by atomic hydrogen. It has been calculated by Elsasser (*loc. cit.*) and gives simply

$$32\pi^2 (2\mu^2 + K^2) / \mu^3 (\mu^2 + K^2)^2, \quad (7)$$

where $\mu = 2Z/a_0$, $K = 2\kappa \sin \frac{1}{2}\delta$, δ being the angle of scattering. We now proceed to the more complicated integral I_3 .

§ 3. *Calculation of Molecular Effect.*—It is natural, in calculating an integral in such an axially symmetric system, to use spheroidal co-ordinates and we will accordingly introduce the co-ordinates ρ_1 , μ_1 , ϕ_1 and ρ_2 , μ_2 , ϕ_2 where ϕ_1 , ϕ_2 are the angles the planes through the nuclei and the points considered make with the plane of incidence, d being the nuclear separation.* First to express $\exp. \{ i\kappa (\mathbf{n}_1 - \mathbf{n}_0) \cdot \mathbf{r} \}$ in these co-ordinates. Any position vector $\mathbf{r}$ is given, in polar co-ordinates, by

$$\mathbf{r} = r (\sin \theta \cos \phi \mathbf{i} + \sin \theta \sin \phi \mathbf{j} + \cos \theta \mathbf{k}),$$

so

$$(\mathbf{n}_1 - \mathbf{n}_0) \cdot \mathbf{r} = r [\sin \theta \{ a \cos \phi + (b - \beta) \sin \phi \} + \cos \theta (c - \gamma)].$$

Now in spheroidal co-ordinates

$$r \cos \theta = \frac{1}{2} \rho \mu d, \quad r \sin \theta = \frac{1}{2} \sqrt{\rho^2 - 1} \sqrt{1 - \mu^2} d.$$

giving

$$\begin{aligned} \kappa (\mathbf{n}_1 - \mathbf{n}_0) \cdot \mathbf{r} &= \frac{1}{2} \kappa d [\sqrt{\rho^2 - 1} \sqrt{1 - \mu^2} \{ a \cos \phi + (b - \beta) \sin \phi \} + \rho \mu (c - \gamma)], \\ &= \alpha \{ \sqrt{\rho^2 - 1} \sqrt{1 - \mu^2} (a_1 \cos \phi + a_2 \sin \phi) + \rho \mu a_3 \}, \text{ say,} \end{aligned}$$

putting

$$\alpha = \frac{1}{2} \kappa d, \quad a_1 = a, \quad a_2 = b - \beta, \quad a_3 = c - \gamma.$$

The volume element dv is now

$$= \frac{1}{8} d^3 (\rho_1^2 - \mu_1^2) d\rho_1 d\mu_1 d\phi_1$$

and I_3 becomes

$$\begin{aligned} &\frac{d^6 e^2}{32} \int_1^\infty \int_{-1}^1 \int_0^{2\pi} \int_1^\infty \int_{-1}^1 \int_0^{2\pi} \left\{ \frac{\rho_1}{d} - \frac{(\rho_1^2 - \mu_1^2)}{r_{12}} \right\} \\ &\quad \times e^{-\rho \rho_1} \exp. \{ i\alpha \sqrt{\rho_1^2 - 1} \sqrt{1 - \mu_1^2} (a_1 \cos \phi_1 + a_2 \sin \phi_1) + \rho \mu a_3 \} \\ &\quad \times (\rho_2^2 - \mu_2^2) d\rho_2 d\mu_2 d\phi_2 d\rho_1 d\mu_1 d\phi_1. \end{aligned} \quad (8)$$

* ρ_1 , μ_1 are defined in the usual manner by $\rho_1 = (r_1 + p_1)/d$, $\mu_1 = (r_1 - p_1)/d$.

We first make use of Neumann's expansion*

$$\frac{1}{r_{12}} = \sum_{\tau=0}^{\infty} \sum_{\nu=0}^{\tau} D_{\tau\nu} P_{\tau}^{\nu}(\rho_1) Q_{\tau}^{\nu}(\rho_2) P_{\tau}^{\nu}(\mu_1) P_{\tau}^{\nu}(\mu_2) \cos \nu(\phi_2 - \phi_1) \left. \begin{array}{l} \rho_2 > \rho_1, \\ \rho_2 < \rho_1. \end{array} \right\}$$

where

$$D_{\tau\nu} = (-1)^{\nu} \epsilon_{\nu} \frac{2\tau+1}{2} \left\{ \frac{\pi(\tau-\nu)}{\pi(\tau+\nu)} \right\}^2, \quad \epsilon_0 = 1, \quad \epsilon_1 = \epsilon_2 = \dots = 2.$$

As ϕ_2 does not otherwise appear in the integrand the only non-vanishing terms will be those from $\nu = 0$. The μ_2 integration is then immediate for the only terms in μ_2 which occur are of the form $(\rho_2^2 - \mu_2^2) P_{\tau}(\mu_2)$ which give on integration

$$\begin{aligned} \int_{-1}^1 (\rho_2^2 - \mu_2^2) P_{\tau}(\mu_2) d\mu_2 &= 2(\rho_2^2 - \tfrac{1}{2}) \quad \tau = 0 \\ &= -4/15 \quad \tau = 2 \\ &= 0 \quad \text{otherwise.} \end{aligned}$$

Substituting in (8) we are left with

$$\frac{d^3 e^2 \pi}{8} \int_1^{\infty} \int_{-1}^1 \int_0^{2\pi} \exp. \{ i\alpha [\sqrt{\rho_1^2 - 1} \sqrt{1 - \mu_1^2} (a_1 \cos \phi_1 + a_2 \sin \phi_1) + \rho_1 \mu_1 a_3] \} \\ \times \{ f_0(\rho_1) + \mu_1^2 f_2(\rho_1) + \mu_1^4 f_4(\rho_1) \} d\rho_1 d\mu_1 d\phi_1, \quad (9)$$

where

$$\begin{aligned} f_0 &= -\frac{2\rho_1 \sqrt{S}}{\rho_1^3} + \rho_1^2 \{ Q_0(\rho_1) + \tfrac{1}{2} Q_2(\rho_1) \} \int_1^{\rho_1} e^{-\rho \rho_1} (\rho_2^2 - \tfrac{1}{2}) d\rho_2 + \rho_1^2 \\ &\quad \times \int_{\rho_1}^{\infty} e^{-\rho \rho_1} (\rho_2^2 - \tfrac{1}{2}) Q_0(\rho_2) d\rho_2 + \tfrac{1}{2} \rho_1^2 (\rho_1^2 - \tfrac{1}{2}) \int_{\rho_1}^{\infty} e^{-\rho \rho_1} Q_2(\rho_2) d\rho_2, \\ f_2 &= -\{ Q_0(\rho_1) + \tfrac{1}{2} (1 + 3\rho_1^2) Q_2(\rho_1) \} \int_1^{\rho_1} e^{-\rho \rho_1} (\rho_2^2 - \tfrac{1}{2}) d\rho_2 \\ &\quad + \int_{\rho_1}^{\infty} e^{-\rho \rho_1} (\rho_2^2 - \tfrac{1}{2}) Q_0(\rho_2) d\rho_2 + \tfrac{1}{2} (1 + 3\rho_1^2) (\rho_1^2 - \tfrac{1}{2}) \int_{\rho_1}^{\infty} e^{-\rho \rho_1} Q_2(\rho_2) d\rho_2, \\ f_4 &= \tfrac{3}{2} Q_2(\rho_1) \int_1^{\rho_1} e^{-\rho \rho_1} (\rho_2^2 - \tfrac{1}{2}) d\rho_2 + \tfrac{3}{2} (\rho_1^2 - \tfrac{1}{2}) \int_{\rho_1}^{\infty} e^{-\rho \rho_1} Q_2(\rho_2) d\rho_2 \quad (10) \end{aligned}$$

Let us now consider the integration for μ_1 and ϕ_1 . We have

$$\begin{aligned} \int_0^{2\pi} \exp. \{ i(b_1 \cos \phi_1 + b_2 \sin \phi_1) \} d\phi_1 &= \int_0^{2\pi} \exp. \{ i\sqrt{b_1^2 + b_2^2} \sin \theta \} d\theta \\ &= 2\pi J_0(\sqrt{b_1^2 + b_2^2}). \quad (11) \end{aligned}$$

* Vide Y. Sugiura, 'Z. Physik,' vol. 45, p. 484 (1927).

Taking $b_1 = a_1 \alpha \sqrt{\rho_1^2 - 1} \sqrt{1 - \mu_1^2}$; $b_2 = a_2 \alpha \sqrt{\rho_1^2 - 1} \sqrt{1 - \mu_1^2}$ gives

$$\int_1^\infty \int_{-1}^1 \exp. (i \alpha \rho_1 \mu_1 a_3) J_0 (\alpha \sqrt{\rho_1^2 - 1} \sqrt{1 - \mu_1^2} \sqrt{a_1^2 + a_2^2}) \{f_0(\rho_1) + \mu_1^2 f_2(\rho_1) + f_4(\rho_1) \mu_1^4\} d\rho_1 d\mu_1. \quad (12)$$

Let $\mu_1 = \cos \eta$, $\alpha a_3 \rho_1 = \mu$, $\alpha \sqrt{\rho_1^2 - 1} \sqrt{a_1^2 + a_2^2} = r$ giving

$$\int_1^\infty \int_0^\pi e^{i u \cos \eta} J_0 (v \sin \eta) \{f_0(\rho_1) + \cos^2 \eta f_2(\rho_1) + \cos^4 \eta f_4(\rho_1)\} \sin \eta d\eta d\rho_1. \quad (13)$$

Now

$$\begin{aligned} \int_0^\pi e^{i u \cos \theta \cos \psi} J_{r-1/2} (z \sin \theta \sin \psi) C_r^r (\cos \theta) \sin^{r+1/2} \theta d\theta \\ = \left(\frac{2\pi}{z} \right)^{1/2} i^r \sin^{r-1/2} \psi C_r^r (\cos \psi) J_{r+r} (z),^* \end{aligned} \quad (14)$$

where C_r^r is a Gegenbauer polynomial defined by

$$(1 - 2h\mu + h^2)^{-r} = \sum_r h^r C_r^r (\mu).$$

Taking $z \cos \psi = u$, $z \sin \psi = v$, so that

$$\tan \psi = v/u, z = (u^2 + v^2)^{1/2}, \quad (15)$$

$r = 0$, $\theta = \eta$ gives

$$\int_0^\pi e^{i u \cos \eta} J_0 (v \sin \eta) \sin \eta d\eta = \sqrt{\frac{2\pi}{z}} J_{1/2} (z).$$

$r = 2$, gives

$$\int_0^\pi e^{i u \cos \eta} J_0 (v \sin \eta) \cos^2 \eta \sin \eta d\eta = \frac{1}{3} \sqrt{\frac{2\pi}{z}} \{-2P_2 (\cos \psi) J_{5/2} (z) + J_{1/2} (z)\},$$

$r = 4$, gives

$$\begin{aligned} \int_0^\pi e^{i u \cos \eta} J_0 (v \sin \eta) \cos^4 \eta \sin \eta d\eta \\ = \sqrt{\frac{2\pi}{z}} \left\{ \frac{8}{35} P_4 (\cos \psi) J_{9/2} (z) - \frac{4}{3} P_2 (\cos \psi) J_{5/2} (z) + \frac{1}{3} J_{1/2} (z) \right\}, \end{aligned} \quad (16)$$

Substituting these values in (12) gives for I_3

$$\begin{aligned} \frac{1}{2} d^5 e^{2\pi^2} \int_1^\infty \frac{1}{\sqrt{z}} [f_0(\rho_1) J_{1/2} (z) + \frac{1}{3} f_2(\rho_1) \{J_{1/2} (z) - 2P_2 (\cos \psi) J_{5/2} (z)\} \\ + \frac{1}{35} f_4(\rho_1) \{8P_4 (\cos \psi) J_{9/2} (z) - 20P_2 (\cos \psi) J_{5/2} (z) \\ + 7J_{1/2} (z)\}] d\rho_1, \end{aligned} \quad (17)$$

* Watson, "Theory of Bessel Functions," Cambridge, 1922, p. 379.

where

$$\begin{aligned} z &= (u^2 + v^2)^{1/2} = \alpha \{a_3^2 \rho_1^2 + (\rho_1^2 - 1)(a_1^2 + a_2^2)\}^{1/2} \\ &= \alpha (a_1^2 + a_2^2 + a_3^2)^{1/2} \left(\rho_1^2 - \frac{a_1^2 + a_2^2}{a_1^2 + a_2^2 + a_3^2} \right)^{1/2} \\ &= \beta (\rho_1^2 - a^2)^{1/2} \quad \text{say,} \end{aligned} \quad (18)$$

and

$$\begin{aligned} \cos \psi &= u (u^2 + v^2)^{-1/2} \\ &= \alpha a_3 \rho_1 z. \end{aligned}$$

The final integration cannot be carried out exactly except for one case, $\delta = 0$, but for high velocity electrons and moderate angles integration by parts gives a satisfactory method of approximation. On substituting the explicit expressions for the Bessel functions and changing the variable to $z' = z/\beta$, the integral takes the form

$$\sin \beta z' (a_0/\beta z' + a_1/\beta^3 z'^3 + a_3/\beta^5 z'^5) + \cos \beta z' (b_0/\beta^2 z'^2 + b_1/\beta^4 z'^4), \quad (19)$$

where the a 's and b 's are lengthy expressions independent of β . Now

$$\begin{aligned} \beta &= \alpha (a_1^2 + a_2^2 + a_3^2)^{1/2} \\ &= \kappa d \sin \frac{1}{2} \delta \quad \text{from (5)} \\ &= 2\pi m v d \sin \frac{1}{2} \delta / h. \end{aligned}$$

For H_2 , $d = \frac{2}{3}a_0 = 0.75 \times 10^{-8}$ cm., $m = 9 \times 10^{-28}$ gm., $h = 6.55 \times 10^{-27}$ erg. sec.; so for electrons of energy of the order 1000 or more volts there is a considerable angular range for δ in which β is sufficiently large to make an expansion in powers of $1/\beta$ of value. We may write this expansion in the form

$$\begin{aligned} &\sin (\beta \sqrt{1-a^2}) (A_s \beta^{-2} + B_s \beta^{-3} + C_s \beta^{-4} + \dots) \\ &+ \cos (\beta \sqrt{1-a^2}) (A_c \beta^{-2} + B_c \beta^{-3} + C_c \beta^{-4} + D_c \beta^{-5} + \dots), \end{aligned} \quad (20)$$

and on carrying out the integration we find

$$A_s = 0 = B_c = C_s = D_c;$$

$$A_c = -\frac{2\sqrt{S}}{\rho^3};$$

$$B_s = \left\{ \frac{3}{7} \frac{\sqrt{S}}{\rho^3} (\log 2\rho + C) - \frac{3}{7} \frac{\sqrt{S}'}{\rho^3} \text{Ei}(-2\rho) + \frac{1}{7} \frac{44\rho + 8\rho^2}{\rho^3} e^{-\rho} \right\} \frac{a^2}{1-a^2};$$

$$\begin{aligned} C_c &= \left\{ \frac{12}{\rho^3} \frac{\sqrt{S}}{\rho^3} (\log 2\rho + C) - \frac{12}{\rho^3} \frac{\sqrt{S}'}{\rho^3} \text{Ei}(-2\rho) \right\} \frac{a^2}{1-a^2} \\ &+ \frac{2e^{-\rho}}{\rho^3} \{(9\rho - 4\rho^2) + a^2(-4\rho + 8\rho^2) + a^4(\rho - 5\rho^2)\} \frac{1}{1-a^2}; \end{aligned}$$

where

$$S' = (1 - \rho + \frac{1}{2}\rho^2)e^{2\rho}, \quad C = 0.5772, \quad \text{Ei}(x) = \int_x^\infty \frac{e^{-t}}{t} dt. \quad (21)$$

We thus have the expansion

$$I_3 = \frac{1}{2}d^5e^2\pi^2 [\cos(\beta\sqrt{1-a^2})\{A_c\beta^{-2} + C_c\beta^{-4} + O(\beta^{-6})\} \\ + \sin(\beta\sqrt{1-a^2})\{B_c\beta^{-3} + O(\beta^{-5})\}]. \quad (22)$$

§ 4. *Discussion of Formulæ. Diffraction.*—We thus obtain for the integral (2) the value

$$2\pi\left(\frac{a_0}{Z}\right)^3 C^2 \left[2 \cos \frac{1}{2}\kappa d (c - \gamma) I + \sqrt{S} \frac{1}{2} \frac{d^5e^2\pi^2 \cos(\beta\sqrt{1-a^2}) A_c}{\beta^2} + \text{etc.} \right]. \quad (23)$$

Let us now examine the significance of this expression for the scattered amplitude. We have

$$\frac{1}{2}\kappa d (c - \gamma) = \frac{\pi mvd}{h} (\cos \chi' - \cos \chi) \\ = \frac{\pi d}{\lambda} (\cos \chi' - \cos \chi),$$

where λ is the wave-length of the electron waves.

Also

$$(1 - a^2)^{1/2} = a_3 (a_1^2 + a_2^2 + a_3^2)^{-1/2}, \\ \beta = \alpha (a_1^2 + a_2^2 + a_3^2)^{1/2},$$

so

$$\beta (1 - a^2)^{1/2} = \alpha a_3 \\ = \frac{1}{2}\kappa d a_3$$

and

$$a_3 = \cos \chi' - \cos \chi \quad \text{from (7)}$$

giving

$$\beta (1 - a^2)^{1/2} = \frac{\pi d}{\lambda} (\cos \chi' - \cos \chi).$$

Hence we have for the scattered amplitude

$$2\pi\left(\frac{a_0}{Z}\right)^3 C^2 \left[\cos \left\{ \frac{\pi d}{\lambda} (\cos \chi' - \cos \chi) \right\} \left\{ 2I + \frac{1}{2} \sqrt{S} d^5e^2\pi \left(\frac{A_c}{\beta^3} + \dots \right) \right\} \right. \\ \left. + \sin \left\{ \frac{\pi d}{\lambda} (\cos \chi' - \cos \chi) \right\} \left\{ \frac{1}{2} \sqrt{S} d^5e^2\pi \frac{B_c}{\beta^3} + \dots \right\} \right]. \quad (24)$$

Thus for fast electrons we have scattering maxima whose positions are defined by

$$d (\cos \chi' - \cos \chi) = n\lambda \quad |n| = 0, 1, 2 \dots$$

the familiar condition for a grating maximum, d being the distance between successive rulings.

§ 5. *Actual Scattering of High Velocity Electrons by Unoriented Hydrogen Molecules.*—Suppose the velocity of the electron beam to be high, so that for moderate angles we may neglect the terms in the above expansion except the first. Then the total scattered amplitude is given by

$$\frac{4\pi^2 m C^2}{h^2} \left(\frac{a_0}{Z}\right)^3 (I_1 + I_2 + I_3) = \frac{\pi^2 m C^2}{h^2} \left(\frac{a_0}{Z}\right)^3 \left\{ \frac{256\pi^2}{\mu^3 K^2} + 48 \left(\frac{a_0}{Z}\right)^3 \frac{d^2 \pi^2}{\beta^2} \right\} \\ \times \cos \left\{ \frac{d\pi}{\lambda} (\cos \chi' - \cos \chi) \right\}. \quad (25)$$

Let us now substitute for μ , κ and β their values

$$\mu = 2Z/a_0, \quad K = 2\kappa \sin \frac{1}{2}\delta = \frac{4\pi m v}{h} \sin \frac{1}{2}\delta, \quad \beta = \frac{d\pi m v}{h} \sin \frac{1}{2}\delta,$$

giving for the amplitude

$$\frac{e^2}{m v^2} \left(\frac{1 + \frac{1}{2}S}{1 + S} \right) \operatorname{cosec}^2 \frac{1}{2}\delta \cos \left\{ \frac{d\pi}{\lambda} (\cos \chi' - \cos \chi) \right\}. \quad (26)$$

We have now to average the scattered intensity over all orientations of the nuclear axes. This may readily be done by choosing $\mathbf{n}_0$ as the axis of a system of polar co-ordinates in which the nuclear axis has direction cosines $\sin \theta \cos \phi$, $\sin \theta \sin \phi$, $\cos \theta$, respectively, the ZOY plane including $\mathbf{n}_1$ and $\mathbf{n}_0$. It is then necessary to evaluate the double integral

$$\int_0^\pi \int_0^{2\pi} \cos(a \cos \theta + b \sin \theta \sin \phi) \sin \theta \, d\theta \, d\phi,$$

where $a = 4d\pi(1 - \cos \delta)/\lambda$, $b = 4d\pi \sin \delta/\lambda$. Using the well-known formulae

$$\int_0^{2\pi} \cos(b \sin \theta \sin \phi) \, d\phi = 2\pi J_0(b \sin \theta), \quad \int_0^{2\pi} \sin(b \sin \theta \sin \phi) \, d\phi = 0,$$

the integral reduces to

$$2\pi \int_0^\pi \cos(a \cos \theta) J_0(b \sin \theta) \sin \theta \, d\theta,$$

and using (14) this is simply

$$2\pi \left(\frac{2\pi}{z} \right)^{1/2} J_{1/2}(z)$$

where $z = (a^2 + b^2)^{1/2} = 2d\pi \sin \frac{1}{2}\delta/\lambda$. As $J_{1/2}(z) = \sqrt{\frac{2}{\pi z}} \sin z$ the averaging

process gives simply

$$\frac{\sin \left(4 \frac{d\pi}{\lambda} \sin \frac{1}{2} \delta \right)}{4 \frac{d\pi}{\lambda} \sin \frac{1}{2} \delta} \approx \frac{\sin x}{x} \text{ say.}$$

The scattering cross section is then approximately

$$\frac{1}{2} \frac{e^4}{m^2 v^4} \left(\frac{1 + \frac{1}{2} S}{1 + S} \right)^2 \operatorname{cosec}^4 \frac{1}{2} \delta \left(1 + \frac{\sin x}{x} \right). \quad (27)$$

This simple expression will hold over a considerable range, but from the method of approximation clearly not below $x = \pi$. On applying the averaging process to the second order term in (24) it is found to vanish, so the above expression will be more accurate than would at first be expected. Below $x = \pi$ a good idea of the form of the curve may be obtained by calculating the value for the case $\delta = 0$, which is completely integrable. Between this point and the first point obtained as above, an idea of the form of curve may be obtained by joining the zero point to the beginning of the calculated curve.

§ 6. *Calculation for case $\delta = 0$.*—In this case the integral I_3 reduces to

$$- \frac{1}{2} d^5 e^2 \pi \int_1^\infty \{ f_0(\rho_1) + \frac{1}{3} f_2(\rho_1) + \frac{1}{5} f_4(\rho_1) \} d\rho_1.$$

and this integration is elementary, giving

$$\begin{aligned} & - \frac{1}{2} d^5 e^2 \pi \left[\frac{\sqrt{S}}{\rho^3} \left\{ -\frac{1}{3} + \frac{2}{5\rho^3} (2\rho^2 + 3\rho + 2) \right\} \right. \\ & \quad \left. - \frac{\sqrt{S'}}{\rho^3} \frac{e^{-2\rho}}{\rho^3} (\rho + 2) - \frac{e^{-\rho}}{\rho^5} (3 + 3\rho + \rho^2) \right]. \quad (28) \end{aligned}$$

Substituting for ρ its value $\frac{3}{2}Z = \frac{1}{4}$ nearly, this becomes 0.04 approximately, so we have a contribution $0.02 d^5 e^2 \pi^2$. Now for $\delta = 0$, I_1 and I_2 reduce to $64\pi^2 \mu^{-5} = 2\pi^2 a_0^5 Z^{-5}$, and so the total scattering cross section becomes

$$\frac{4m^2 \pi^4}{h^4} \left(\frac{a_0}{Z} \right)^6 \left\{ C^4 \left(\frac{8\pi^2 a_0^5 e^2}{Z^5} + 0.02 d^5 e^2 \pi^2 \right)^2 \right\},$$

and as $d = \frac{3}{2}a_0$, $Z = \frac{1}{4}$ we may write this

$$\left(\frac{4\pi^2 m}{a_0^2 h^2} \right)^2 2 \times 0.8, \quad (29)$$

i.e., the scattering is 0.8 that for 2 hydrogen atoms.

Using formulæ (27) and (29) the cross sections as a function of angle of

scattering for 10,000 and 420 volt electrons have been calculated giving the curves illustrated in fig. 2. In both cases the portion from A to B is obtained

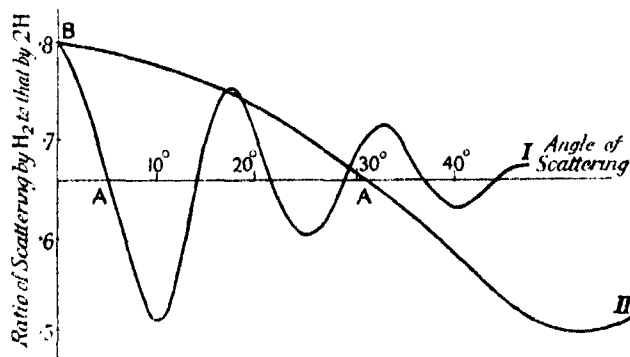


FIG. 2.

merely by continuation of the curve to meet the axis at the known point B.* For convenience of scale cross sections are given as ratios of the corresponding ones for atomic hydrogen. These differ not only in the diffraction effects but also in the fact that the molecular wave functions contain an atomic number Z which is not unity but 1.166 .†

§7. *General Remarks.*—The diffraction effects which have thus been shown to occur would be very difficult to detect experimentally owing to the smallness of the peaks relative to the “atomic” background. However it is clear that for any system of atoms possessing structural symmetry these diffraction effects will be obtained, and Mark and Wierl‡ have obtained excellent diffraction rings with methane using 36,000-volt electrons. At these velocities just as above, nuclear scattering will predominate throughout the secondary maxima and simplified theories based on the scattering of waves from a symmetrical system may be applied. Throughout this discussion the effect of nuclear rotation and vibration has been neglected; that this is permissible is clear from the fact that a molecule is effectively rigid to a 20,000-volt electron, the

* In the case of curve II the portion AB has been obtained by magnification of a curve of the same proportions as I, but no great accuracy can be claimed for its detailed shape. However, it must be approximately correct.

† As the actual values of the ratios given in the curve depend so much on the value of Z , no great accuracy can be claimed for them, though it is clear that the scattering by H_2 will not differ much from that for atomic hydrogen, the rate of fall off with angle being somewhat steeper initially than for the latter.

‡ ‘Naturwiss,’ vol. 18, p. 205 (1930).

latter moving across the molecular diameter before any appreciable non-rigid body motion has taken place. However, when necessary, the effects of such motions may always be brought in by calculating the scattered amplitude as a function $f(\theta, \phi, d)$ of the orientation angles θ, ϕ of the molecule and the distance d between the nuclei. If this function is $f(\theta, \phi, d)$ the observed cross section will be obtained by calculating

$$\left| \int_0^\pi \int_0^{2\pi} \int_{-\infty}^{\infty} f(\theta, \phi, d) \chi(\theta, \phi) \bar{\chi}(\theta, \phi) \zeta(d) \bar{\zeta}(d) \sin \theta d\theta d\phi dd \right|^2,$$

where $\chi(\theta, \phi)$ is the rotational wave-function of the molecule, $\zeta(d)$ the vibrational function. The fact that the scattering probability does depend on θ, ϕ, d leads to a finite probability of energy interchange between the incident electron and the molecular rotation and vibration, an effect of importance in the case of slow electrons. Owing to the failure of Born's theory for slow electrons it is not at present possible to determine the cross sections in such cases and for the same reason no attempt has been made to expand the integral (17) above in powers of the velocity, for such an expansion would be valid only where the theory fails.

Summary.

The scattering cross sections presented by hydrogen molecules to electron beams are calculated using Born's Theory of Collisions. The results show that diffraction effects are to be expected and the intensities of these phenomena determined.

Energy Losses of Electrons in Nitrogen.

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Introduction.

Critical potential measurements in nitrogen have been published by several investigators.* In most of this work the excitation and ionisation potentials were located by the sudden changes in the current to a detecting electrode, produced by photoelectrically active radiation or by positive ions as the accelerating voltage was raised above the critical value. Recently a good deal of information has been secured by the application of positive ray analysis† and by combined electric and spectroscopic observations.‡ In an extensive study of the scattering of electrons and ions in gases at rather high pressures Langmuir and Jones§ have measured energy losses of electrons by a kind of retarding potential method. Harnwell|| studied the angular distribution of scattered electrons in a number of gases; by means of a radial, inverse first power, electrostatic field, in which the electrons were deflected through 90°, he was able to measure the velocity of the electrons after scattering. He found a broad maximum in the distribution curves for nitrogen, indicating inelastic collisions with a most probable energy loss of some 12·9 volts. No other direct measurements of the energy losses in single collisions in nitrogen appear to have been made.

The present investigation is an attempt to measure with a higher accuracy the energy given up by electrons at inelastic impacts in nitrogen under such conditions that no appreciable amount of multiple collisions should occur. Only collisions for which the resulting deflection of the colliding electron from the original line of flight is very small can be studied with the apparatus used.

* For a review of work previous to 1926, *vide* Franck and Jordan, 'Anregung von Quantensprüngen durch Stösse,' p. 267, Berlin, 1926. Cf. Levesley, 'Trans. Faraday Soc.,' vol. 23, p. 552 (1927).

† Hogness and Lunn, 'Phys. Rev.,' vol. 26, p. 786 (1925); Dorach and Kallman, 'Z. Physik,' vol. 44, p. 565 (1927).

‡ Duncan, 'Astrophys. Journ.,' vol. 62, p. 145 (1925); Sponer, 'Z. Physik,' vol. 34, p. 622 (1925); Kneser, 'Ann. Physik,' vol. 79, p. 597 (1926); Kondratjew, 'Z. Physik,' vol. 38, p. 346 (1926); Turner and Samson, 'Phys. Rev.,' vol. 34, pp. 743, 747 (1929).

§ 'Phys. Rev.,' vol. 31, p. 357 (1928).

|| 'Phys. Rev.,' vol. 33, p. 559 (1929).

Earlier critical potential work has almost entirely been devoted to the outermost electronic levels, whilst very few determinations of critical potentials for the soft X-ray levels of gases have been published. Mohler and Foote,* however, using the photoelectric method, found breaks in nitrogen from which they concluded that the ionisation potential for the K-level of the molecule is 374 volts. In view of the poor critical potential data for this level it was thought that a study of the region of energy loss corresponding to transitions from the K-level would be of particular interest. Also, a determination of the energy loss by the method of the present work would be expected to yield a more accurate value than the usual photoelectric method, when applied to such high critical potentials.

Method.

The method of velocity analysis adopted in this work is similar to that of Harnwell, in that it is based on the deflection of electrons in a radial, first power, electrostatic field, such as is obtained by the use of two oppositely charged electrodes forming part of a cylindrical condenser. It is very desirable to use electrostatic deflection, instead of the usual magnetic one, notably in work on gases where it is mostly necessary to make the electrons travel through a considerable distance in the gas outside the deflection chamber; when magnetic deflection is employed, it is very difficult to guard the electrons from the influence of stray fields during this passage. In Harnwell's apparatus a narrow beam of electrons was defined by two narrow slits, placed a distance apart, and the beam subsequently deflected electrostatically through 90° into a receiving box. The present investigation utilises the divergent beam from a single slit, which is deflected electrostatically through about 127° and at the same time concentrated on a second slit, placed in front of the receiving box. The theory of this method was developed by Hughes and Rojansky† and the results confirmed experimentally by Hughes and McMillen.‡ Consider an electron which is projected into such a radial electrostatic field in a direction parallel to the surfaces of the deflecting plates at the point where it enters the field (I in fig. 1). In the following we are only concerned with the velocity component normal to the cylinder axis O of the electrodes, since the effect of any component parallel to this axis is merely to turn the path into a helix, the motion along this axis being unaffected by the field as

* 'Bur. Stand. Sci. Pap.,' No. 425 (1922); cf. also Compton and Mohler Bull. Nat. Res. Council, vol. 9, Pt. 1, No. 48 (1924).

† 'Phys. Rev.,' vol. 34, p. 284 (1929).

‡ 'Phys. Rev.,' vol. 34, p. 291 (1929).

in the magnetic case. If the initial velocity is v_0 corresponding to a fall through a potential difference V_0 volts, the electron will be bent into a circular path with its centre on the axis provided that

$$eE = mv_0^2/r = 2eV_0/r, \quad (1)$$

where E is the deflecting field. Since this is equal to $V/r \log r_2/r_1$, if V is the potential difference between the electrodes of radii r_1 and r_2 respectively, the condition (1) upon reduction takes the form

$$V/V_0 = 2 \log r_2/r_1. \quad (2)$$

By virtue of (2) we may measure the velocity of any electron by the corresponding deflecting voltage $V' = 2 V_0 \log r_2/r_1$.

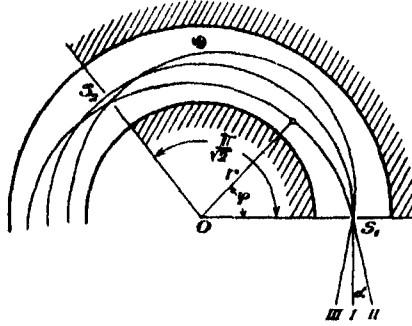


FIG. 1.

To find the path in polar co-ordinates r, ϕ round the axis in the general case, when V may be different from V' and when the initial direction differs from the parallel one by an angle α , the differential equation for the path

$$\frac{d^2 u}{d\phi^2} + u = \frac{V}{V' r_0^2 \cos^2 \alpha} \cdot \frac{1}{u}. \quad (3)$$

$u = 1/r$, has to be solved, subject to the boundary conditions $u_0 = 1/r_0$ and $\left(\frac{du}{d\phi}\right)_0 = -\frac{1}{r_0} \tan \alpha$. Hughes and Rojansky, applying a method of successive approximations, obtained as a first solution

$$r_0 u = c + (1 - c) \cos \sqrt{2} \phi - \frac{1}{\sqrt{2}} \sin \sqrt{2} \phi \tan \alpha, \quad (4)$$

where $c = \frac{1}{\cos \alpha} \sqrt{\frac{V}{V'}}$. Equation (4) shows that to this approximation, i.e., for small values of α , refocussing of all the different electron paths, starting

from r_0 , 0 takes place at a point $\phi = \pi/\sqrt{2} = 127^\circ 17'$, $r = r_0/(2c - 1)$. The resolving power is given by

$$\frac{r - r_0}{r_0} = \frac{\Delta r}{r_0} = \frac{\Delta V_0}{V_0}, \quad (5)$$

where ΔV_0 measures the small change of energy of the electron corresponding to the shift Δr of the focus along the radius $\phi = \pi/\sqrt{2}$. From the second approximation to (3) it could be shown that the spread of a homogeneous electron beam at $\phi = \pi/\sqrt{2}$ due to the finite angular width α at s_1 is determined by $s = \frac{4}{3} r_0 \alpha^2$ and is directed toward the inside of the circle from the focus for $\alpha = 0$. This shift is illustrated by paths II and III in fig. 1 for two unusually large values of α . These curves are taken from the paper by Hughes and Rojansky, who computed the paths by numerical integration.

In any actual experimental arrangement based on this principle there must be an apparent latitude, ΔV_0 , of the measured energy of a strictly homogeneous electron beam, which is determined by the magnitude of α and the finite dimensions of the slits. It is easy to see that the whole of this apparent energy distribution will be contained in the interval

$$\frac{\Delta V_0}{V_0} = \frac{4}{3} \alpha^2 + \frac{1}{2} \left(\frac{l_1 + l_2}{\pi r_0} \right)^2 + \frac{\epsilon_1 + \epsilon_2}{r_0}, \quad (6)$$

if the length and width of the two slits are l_1, l_2 and ϵ_1, ϵ_2 respectively. Obviously the uncertainty in the energy determination will only be a fraction of this.

Measurements of energy loss have the advantage that the results are uninfluenced by contact potential differences between the source of electrons and the other electrodes, as long as these potential differences remain constant during the whole time of an experiment. This is due to the circumstance that the loss is counted from the measured energy of those electrons which have made no, or only elastic, collisions but which are affected by contact potential differences just as the others. Obviously, a constant contact potential difference between the deflecting electrodes is without influence provided that $2 \log r_2/r_1$ in equation (2) is determined by calculation from the geometry of the apparatus. However, in view of the difficulty of calculating the effect of the other metal parts at both ends of the deflecting plates (fig. 3a) it appeared better to determine this constant by experiment. In this case, constant contact potential differences will, of course, affect the result, although the error introduced is very small where the applied potentials are comparatively high, as in the present experiments.

All this refers to measurements in which the primary voltage accelerating the electrons into the gas is kept constant and the energy distribution determined by the application of a series of different voltages across the deflecting plates, which in turn bring the electrons corresponding to different parts of the distribution curve into the receiver. A modified method has been used for the small energy losses, the results of which are entirely independent of constant potential differences. In this case both bombarding voltage and deflecting voltage are kept sensibly constant. After the electrons have traversed the gas, however, they are accelerated by a small, accurately measured potential difference before they enter the deflection arrangement. By varying this potential difference it is possible to direct electrons which have lost any amount of energy to the receiver and thus obtain an immediate measure of their energy loss.

Apparatus.

The experimental arrangement adopted is shown in figs. 2 and 3. The box D, containing the deflecting device, is placed in the main part of the large glass apparatus. It is rigidly attached to a wide central tube projecting from the glass stopper, which closes the wide main tube at the bottom. This central tube also serves for the rapid evacuation of the inside of the box. The box is made of brass, carefully silver-soldered. The walls carrying the slits S_1 and S_2 and the bottom to which the deflecting plates are fixed were made of thick brass plates to give high rigidity. The upper rim of the box is provided with a plane flange to which the lid is fastened with a number of screws. The deflecting plates consist of two bent pieces of thick brass, carefully machined to the required shape. The radius of the middle path is 35.0 mm., the curvatures of the two oppositely charged surfaces being 33.0 and 37.0 mm. respectively. The way in which the deflecting electrodes are mounted in the box will be seen from fig. 3b. There are two such brass holders as the one shown in this figure, which are fastened by screws to the bottom of the box. The electrodes are insulated from the holders by mica. The small brass prisms separating the plates are in contact with the holders. They are wedge-shaped, in order to cause the smallest possible disturbance of the deflecting field in the middle part. The final adjustment of the distance separating the plates was made by altering the thickness of the mica insulation between the prisms and the plates, the distance being checked by a measuring microscope for a number of different points along the arc at the upper and lower boundaries of the plates. The mean distance was found to be 4.03 mm. with a mean deviation of 0.04 mm. This was due to a slight systematic error at one end ;

over the greater part the variation was considerably less than this. The distance would probably have shown a still better constancy in the middle

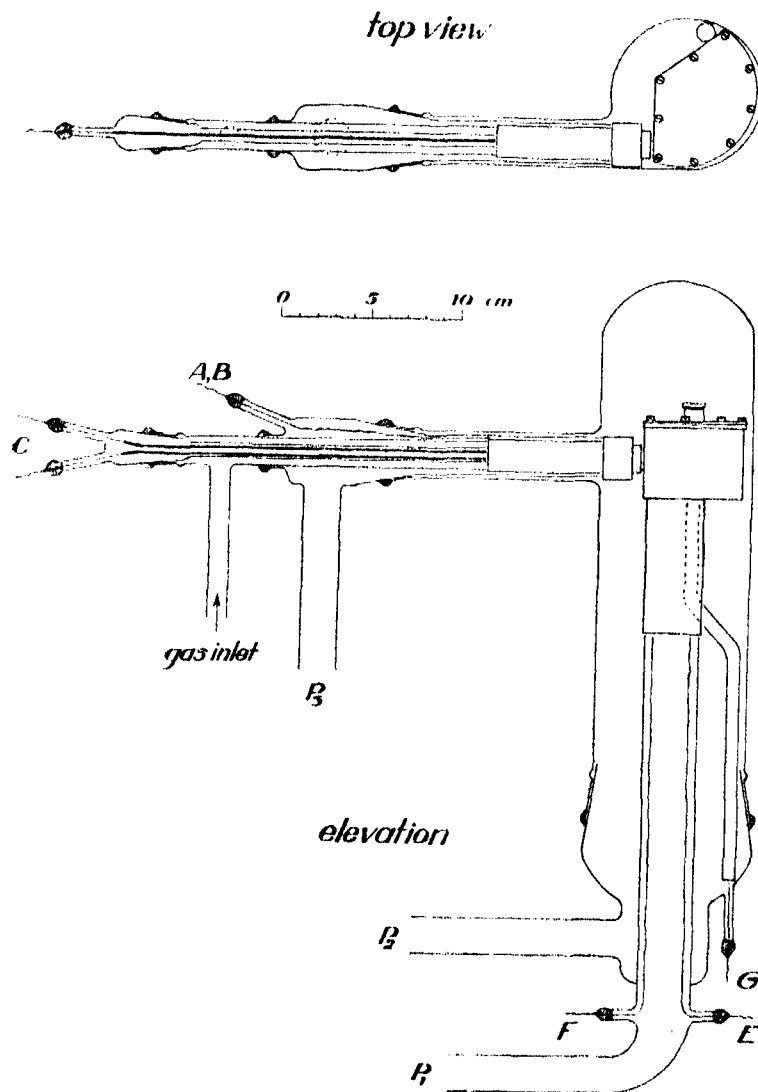


FIG. 2.

part, where the trajectories of the electrons fall. Fig. 3c exhibits the construction of the slits S_1 and S_2 . The object of giving them this peculiar shape is to disturb the deflecting field as little as possible at the points where the

electrons enter and leave the field. The slits are made of thin sheet copper; the openings, 0.1×3 mm., were cut with a razor blade. From the dimensions

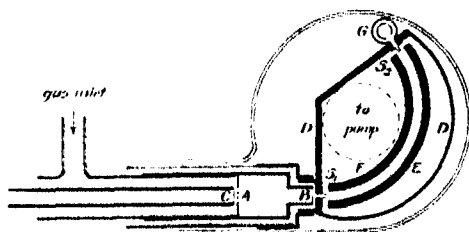


FIG. 3A.

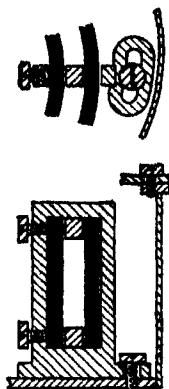


FIG. 3B.

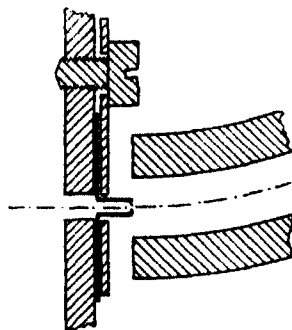


FIG. 3C.

of the slits and the deflecting condenser the apparent latitude of determination is by (6)

$$\Delta V_0 = (0.0020 + 0.0015 + 0.0055)V_0 = 0.009V_0. \quad (7)$$

The collector, G in fig. 3a, is completely shielded by a long brass tube soldered to the box and closed at the upper end by a brass button, the lower end being closed up by the quartz tube carrying the collector. The collision chamber and the electron source are mounted by means of tight-fitting brass caps on three glass tubes occupying a side arm of the main tube. Electrons from C are accelerated through the perforated anode A into the field-free space bounded by A and B, where they make collisions with the gas molecules. B is a thin platinum foil, silver-soldered to the end of the brass jet shown in the drawing. It is perforated with a number of small holes of diameter 0.09 mm. Between B and the box D the auxiliary accelerating voltage is applied. In some of the experiments the cathode C, which is placed within 2 mm. of A,

was a tungsten filament. It was found more convenient, however, to use a short strip of platinum foil covered with a mixture of strontium and barium oxides obtained by evaporation from a solution of the corresponding nitrates. This gave a sufficient and rather steady emission at a dull red heat, so that the voltage drop across the strip could be kept low—0.5 volts, as measured outside the tube. With gas in the apparatus, however, the cathode is subjected to bombardment by positive ions diffusing out from the region between A and B, when the tube is working, and due to this bombardment the active layer is gradually consumed. It is therefore necessary to renew the deposit fairly frequently, and for this reason the cathode has been mounted on a separate glass stopper. The alignment of the several parts is a somewhat lengthy procedure. With a little care, however, it was possible to soften the sealing-wax joints with a flame, sufficiently to permit a slight shift of the stoppers when acted upon, without letting air into the tube. This saved much time.

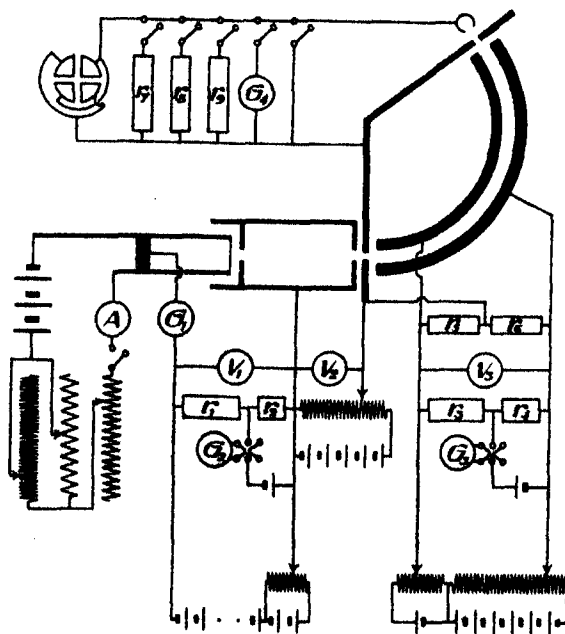


FIG. 4.

A diagram of the essential electrical connections is shown in fig. 4, where the metal parts of the tube are indicated by heavy lines. It will be seen that the cathode foil is shunted, outside the tube, with a suitable resistance and the bombarding voltage applied between the middle of this resistance and the anode. In a similar way it has been arranged that the potentials of the

deflecting electrodes will always be symmetrical with respect to the potential of the box and the slits, whatever the deflecting voltage. The two equal resistances r_5 and r_6 are 50,000 ohms each. In each case a suitable combination of resistances of different magnitude (of which mostly only one or two are indicated in the diagram) serve for the accurate adjustment of the bombarding, the deflecting and the auxiliary accelerating voltage. The constancy of the two first-mentioned voltages can be checked continuously by sensitive compensation circuits comprising the high resistances r_1 , r_2 and the galvanometer G_2 in the one case, and r_3 , r_4 and G_3 in the other. For the measurement of the current received by the collector a quadrant electrometer of sensitivity 2000 mm. for 1 volt is used, which may be shunted by the high resistances r_7 , r_8 or r_9 ; for the largest currents a very sensitive galvanometer G_4 may be used. The range of current sensitivity which is covered by the whole arrangement is from 4.2×10^{-15} to 3.7×10^{-11} amps./div., with the distances of the scales that were chosen.

The gas to be investigated is introduced into the collision chamber through the inner tube, as shown in fig. 3A. Pure nitrogen was prepared from ammonia vapour, which was oxidised over glowing copper oxide in a long narrow tube. Traces of oxygen, if present, were removed by passing the gas over glowing copper. Water vapour and ammonia were then absorbed by bubbling the gas through a series of wash bottles containing first dilute, and later concentrated sulphuric acid. The nitrogen was finally stored in a large bulb in contact with phosphorus pentoxide. With the exception of two sealing-wax seals where the hard glass tube for the copper oxide and copper tube was inserted, the whole nitrogen generating system consisted of glass blown together.

All experiments on nitrogen were made with the gas continuously flowing through the tube. From the large container the nitrogen passed an artificial leak—an ungreased stop-cock with a gradually diminishing groove ground in it, the whole being closed from the outer atmosphere by a small mercury cup—by means of which the pressure could be adjusted to the desired value as measured by a McLeod gauge, connected to the line close to the apparatus. Before entering the apparatus the gas had to pass a cooled mercury trap. From the collision space the gas diffused through the slit S_1 into the deflection chamber, and through the narrow space between the metal caps guiding the side tubes, into the space surrounding the box. In both cases the gas was rapidly pumped off by fast diffusion pumps connected through wide tubing at P_1 and P_2 in fig. 2. In this way the pressure in the deflecting chamber could be kept at a value about 1/50th of that in the collision space. It was

originally intended to improve this ratio further by using a third pump at P_3 to step down the pressure between B and S_1 in fig. 3a. The double-walled side tube was introduced for this purpose. When the arrangement was tried, however, it was found that the decrease in pressure inside the deflection chamber, when the pump at P_3 was started, was very small. In the following measurements, therefore, only the pumps at P_1 and P_2 have been used.

The pressures of nitrogen that have been used range from 1.0×10^{-2} to 4.0×10^{-2} mm. as measured by the McLeod gauge. Since the nitrogen was not restored to the container after passing through the pumps, there was a slight gradual decrease in pressure in the course of a series of measurements, the pressure at the end of a run being about 5 per cent. lower than at the start. The values given are mean values from two such measurements. The total bombarding current varied from 24 to 640 microamps. in different experiments. The highest bombarding voltage used is 587 volts. Below 80 volts no satisfactory measurements have been obtained.

Results.

Unless otherwise stated, all the distribution measurements which will be considered in the following were obtained with the method of the auxiliary accelerating field, as described above. The procedure of taking a curve was as follows. After the bombarding current and the primary voltage had been adjusted to the chosen values, the latter one balanced against the cell of the compensation circuit, a suitable value of the deflecting voltage, which would bring the primary electrons into the collector, was found by trial with the electrometer free to swing. This was done with a small accelerating voltage—usually about 2 volts—between B and S_1 . Pressure and conditions in general being steady, the measurements were then started and a series of readings taken for different accelerating voltages from 0 volts upwards. No measurements have been taken by this method with an accelerating potential above 30 volts. Although the applied voltages between cathode and anode and across the deflecting plates are kept sensibly constant during the whole of an experiment, it is necessary to make certain that the position of the primary peak on the scale of the auxiliary voltage does not shift by any greater amount during an experiment. Such a shift may be produced by an unsteady contact potential difference between the cathode and the slit S_1 , due to changes in the composition or resistance of the cathode surface or to contamination of the slit by sputtered matter from the discharge. Further there is the possibility of some change in the contact potential difference between the deflecting

plates. A shift of the electron emitting spot over the surface of the cathode would not be very serious with the small potential drop that was necessary for heating the foil. The position of the primary peak was always checked at the end of a run. In the beginning the peak was very often found to have suffered quite a large shift, sometimes 1 volt or more, which made the measurements valueless. Experiments showed that the peak would continue to shift in the same direction for several hours, mostly quite gradually; the total shift was then sometimes a couple of volts. Many alterations were tried and much time was wasted in attempts to find the source of this disturbance. Finally, after the whole apparatus had been taken to pieces and thoroughly cleaned in strong nitric acid, the trouble disappeared. I believe that some contamination at the slit edges must have been the cause of the unsteady potentials. After this the positions of the primary peak before and after taking a curve seldom differed by more than 0.2 volts. Where a shift of this order has been found I have corrected the curve, assuming the shift to have been gradual and uniform over the interval of time required for the measurements.

There was frequently a change by as much as 20 or 30 per cent. in the magnitude of the currents for the primary peak before and after a run. This is easily explained as due to small displacements of the electron source perpendicular to the direction of the electron beam, since the alignment of the source and slits is necessarily rather sensitive to such displacements. Although it is rather likely that these changes affect the rest of the distribution curve in the same direction, I have considered it better not to apply any more or less uncertain correction for this change. The height of the primary peak shown in the curves, which are reproduced in the following, is always the mean of the measurements obtained before and after the corresponding distribution curve was taken.

Some typical examples of the distribution curves obtained in this way are shown in figs. 5 to 8. In all curves the peak due to primary and elastically scattered electrons is to the left in the figure; it has been reduced in the scale $1/50$ or $1/100$ for convenience. The scale at the bottom of each curve gives the auxiliary accelerating voltage, measured from the position of the primary maximum, i.e., the energy loss in volts of the corresponding electrons.

The most outstanding feature of these distributions is the sharp peak appearing for a loss of nearly 13 volts. This is present, with the same definite appearance, in all the curves that have been measured. Besides this peak there are several smaller maxima or indications of maxima in the curves,

particularly in those where the resolving power was not too much reduced by a high bombarding voltage. At least some of these maxima appear to be

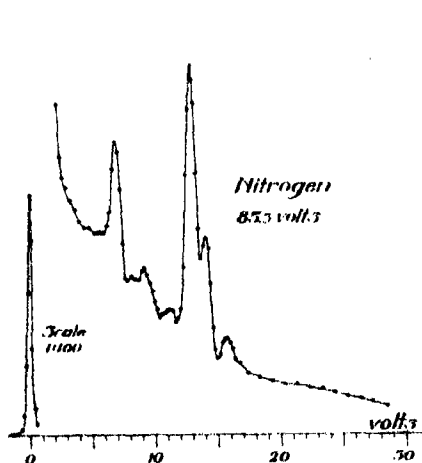


FIG. 5.

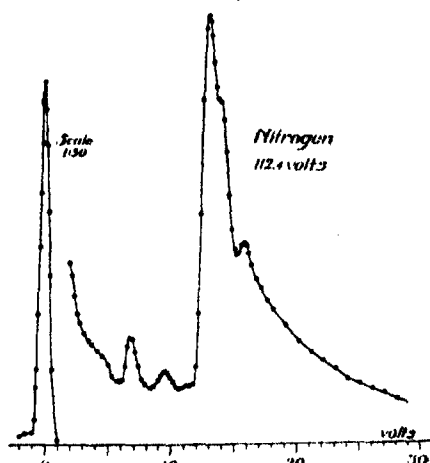


FIG. 6.

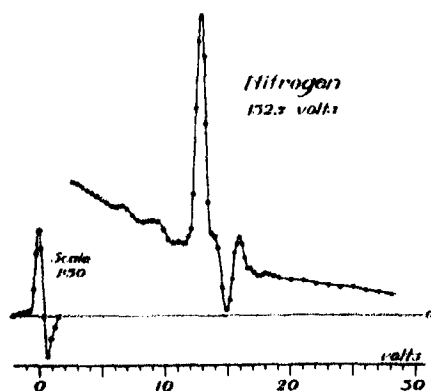


FIG. 7.

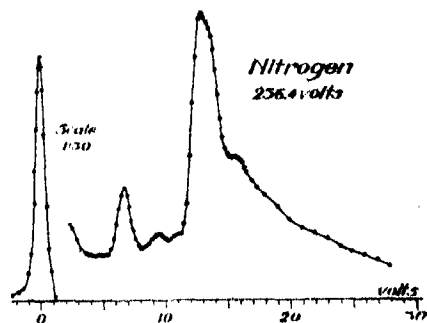


FIG. 8.

considerably broader than the 13-volt peak. All the maxima are superposed on a continuous distribution of electrons. At least part of this distribution in the region of higher losses, above 15 volts, must be related to the sharp peak and adjoining small maxima on the side of higher losses.

Not all features of these distribution curves are due to the presence of nitrogen in the tube. Part of the inelastic collisions responsible for the observed distribution of energy take place at the edges of the entrance slit S_1 and of the small holes in B (fig. 3a). To a small extent collisions with A

could also possibly contribute to the measured currents. To discriminate between effects of different origin I have taken several blank runs with a high vacuum in the tube, measuring the distribution in the same way as when there was gas present. From a comparison of the curves so obtained with those measured in the presence of nitrogen, and also from a study of the changes in the curves when different pressures are used, it has mostly been possible to distinguish the effects of collisions with the electrodes from those produced by impacts with molecules of the gas.

A few words must be said in connection with fig. 7. It will be seen that in this experiment quite strong currents of reversed sign were obtained for a narrow region of accelerating voltages just above the primary peak. Also, there is an unusually deep depression of the curve to the right of the prominent 13-volts maximum, which appears to be due to a similar effect. The same kind of thing, although usually less marked, occurred in some of the other curves obtained. The explanation would seem to be that in these experiments the alignment of the electron source and slit must have been less perfect, so that the bulk of the electrons entered the deflecting condenser with a direction of travel differing by a finite angle α from the normal to the radius. For the appropriate value of the auxiliary voltage these electrons must still be able to enter the collector G, but when they are slightly more accelerated they strike the outer edge of the slit S_2 under such incidence that a large fraction is reflected on to the outer surface of one wing of the collector G. For electrons of this velocity it is known that the secondary emission of slow electrons usually exceeds the bombarding current, especially if the metal is struck at oblique incidence. The secondary electrons from the outside of the wing escape to the surrounding metal wall and thereby give rise to the apparent positive current to G recorded by the electrometer. It is in agreement with the proposed explanation that the minimum is very sharp, since the mechanism depicted could only be expected to work when the electrons are focussed within a very small region of the outer slit edge. The voltage separation of the peak and the accompanying minimum is slightly greater than the value corresponding to the slit width, but this is only what would be expected, if the width of the peak is determined to a considerable extent by other factors than the dimensions of the second slit alone. It is evident that the presence of this minimum accompanying each maximum has enhanced some of the maxima in the curves. It is unlikely, however, that any spurious maxima due to this cause could have been found and included in the following results.

In Table I are collected the data for the positions of the maxima in the

different distribution curves, measured in terms of energy loss (in volts). Bombarding voltage, total current in 10^{-5} amps. and pressure in 10^{-3} mm. are also stated in each case.

Table I.

No.	Voltage.	Current.	p.	V_1 .	V_2 .	V_3 .	V_4 .	V_5 .	V_6 .	V_7 .
24	85.3	64.1	15.3	6.75	9.05	11.00	12.75	13.95	15.75	—
47	85.7	7.83	34.3	7.05	9.50	—	13.00	14.15	15.90	—
34	88.3	64.1	11.3	6.50	9.15	10.15	12.70	14.00	15.60	18.2
33	92.5	64.1	11.4	6.80	9.15	10.00	12.65	13.75	15.45	—
31	94.0	64.1	12.6	6.65	9.20	—	12.65	13.80	15.70	—
30	100.0	64.1	12.5	6.90	9.00	—	12.75	14.05	15.55	—
17	103.8	35.6	9.8	6.80	9.50	—	12.60	13.90	15.90	—
46	110.8	7.83	37.6	6.65	9.10	—	12.70	13.75	15.80	—
25	112.4	64.1	15.0	6.75	9.50	11.10	12.95	14.00	15.80	—
29	120.5	28.5	13.0	6.25	9.10	—	12.65	14.00	15.60	—
23	131.5	64.1	17.9	6.40	9.20	10.85	12.70	13.85	15.75	—
41	132.7	7.83	36.6	6.60	9.25	10.85	12.80	13.95	15.95	18.05
18	137.0	64.1	14.9	6.80	9.30	—	12.95	14.05	15.90	—
26	147.6	64.1	13.5	6.50	9.15	10.90	12.85	14.10	15.80	—
39	160.1	7.83	36.5	—	9.50	—	12.90	14.10	16.00	18.1
27	160.2	35.6	12.7	6.40	9.15	11.00	13.00	14.00	15.95	—
16	172.9	4.35	11.1	6.50	9.00	—	12.50	13.90	15.65	—
28	192.9	28.5	14.0	6.05	—	—	12.95	—	16.00	—
40	200.0	7.83	38.9	6.70	9.25	—	12.70	—	16.10	18.45
22	211.9	64.1	19.4	6.60	9.30	—	12.70	13.60	15.80	—
21	236.4	64.1	20.6	6.55	9.60	10.95	12.75	13.70	15.95	—
45	261.9	5.20	32.1	6.95	9.25	—	12.85	—	16.25	—
44	315.9	5.20	32.8	—	9.10	—	12.85	—	—	—
43	369.1	5.20	34.9	6.85	9.40	—	12.85	—	15.80	17.35
Mean				6.64	9.25	10.86	12.78	13.93	15.82	18.03

The measurements on the maxima, when no nitrogen was present in the tube, are given in Table II. It should be stated that, with the exception of the maximum near 6.8 volts, the maxima found are very small and diffuse.

Table II.

No.	Voltage.	Current.	V_{01} .	V_{02} .	V_{03} .	V_{04} .
48	93.7	7.83	6.85	9.80	—	—
36	139.1	7.83	6.75	9.40	10.55	12.85
37	160.0	2.35	6.70	—	—	—
49	208.2	0.59	6.80	—	10.70	13.45
Mean			6.78	9.60	10.63	13.15

To facilitate the following discussion of the results the mean values for the different maxima derived from Table I are collected in Table III, together

with the number of independent determinations in each case. The average error in each single determination, obtained in the usual way, is also included in this table. It would be easy to calculate from these data the probable error in the mean values by the usual error calculus. This gives values as small as 0.03 volts in the most favourable cases. It is believed, however, that the average error tabulated in Table III offers a more reliable picture of the accuracy in the present case. It must be remembered that the single determinations in Table I are only given to 1/20th of a volt. Finally, Table III contains some data from other work for comparison in connection with the interpretation attempted below.

Table III.

	V ₁ .	V ₂ .	V ₃ .	V ₄ .	V ₅ .	V ₆ .	V ₇ .
No. of determinations	22	23	9	24	19	23	5
Average error	±0.24	±0.17	±0.28	±0.13	±0.15	±0.19	±0.42
Maximum	6.64	9.25	10.86	12.78	13.93	15.82	18.03
Interpretation	Pt 6.5 Cu 6.9	a(2) 8.91 a(3) 9.11 a(4) 9.31 a(5) 9.50		b 12.52 b 12.79 c 12.87-8			

Discussion.

It is evident from Table II that at least part of the first maximum, V₁, must be attributed to impacts with the electrodes. The sharpness and general appearance of this maximum is on the whole the same, whether nitrogen is present in the tube or not, so that it seems likely to be due to the electrodes entirely. It is interesting to mention that in some previous work* on energy losses by electrons scattered from solids, I found that there is frequently a loss of 6.5 volts for platinum as the scattering substance, and of 6.9 volts, when the scatterer is of copper. The apparatus used in obtaining these results was of a different type, employing magnetic deflection. It is possible that the maximum found in the present investigation is a blend of the Pt maximum, due to the platinum foil B, and the Cu maximum deriving from the copper slit S₁. The slight difference between the mean values with and without gas in the apparatus, could possibly indicate that the proportions of each one are slightly different in the two cases. The sharpness of the V₁ maximum is, however, remarkable; it is decidedly sharper than in the previous investigation referred to. The fact that the incidence on the scattering surface is

* 'Proc. Roy. Soc.,' A, vol. 127, p. 111 (1930).

grazing in the present experiments may have some significance in this connection. The other maxima listed in Table II are so small and diffuse that it is difficult to say whether they should be attributed to the electrodes themselves or to traces of nitrogen adsorbed on the electrodes—the tube was not degassed by heating between the measurements with and without nitrogen. The latter of these two alternatives is probably the correct one in the case of V_{02} ; as indicated by the numbers of the series the electrodes had been bombarded in vacuum for a longer lapse of time in the two last runs of Table II. The corresponding maxima being small and somewhat uncertain in both cases it is not possible to decide whether V_3 of Table III is identical with V_{03} for the vacuum curves. The other maxima in Table III are not due to collisions with the metal parts of the tube.

Leaving out of consideration the two maxima V_3 and V_7 , for which the number of independent determinations is comparatively small and which are rather diffuse in the curves where they show up, I think that at least V_2 , V_4 , V_5 and V_6 belong to collisions in the gas. By far the most conspicuous one of these is V_4 . An energy loss of 13.0 volts in nitrogen has previously been diagnosed by Langmuir and Jones (*loc. cit.*) from an analysis of the current-voltage characteristics of a special type of discharge between a wire cathode and a surrounding cylindrical anode. Harnwell (*loc. cit.*) found a maximum of inelastic collisions, corresponding to a loss of 12.9 volts, in the course of a study of the angular scattering of electrons in different gases; for this work it was necessary to use an apparatus of lower resolving power than in the present experiments. The curves for nitrogen published by Levesley*—who used the method, developed by Hertz,† of measuring the fraction of very slow electrons present—appear to me to give indications of an energy loss of about the same magnitude, although this is interpreted by Levesley as due to multiple collisions. There is also a maximum of very slow electrons for a bombarding voltage of 9.0–9.9 volts in his curves. Earlier critical potential work has mostly yielded values from 7 to 9 volts for the “resonance” potential of nitrogen.

Fig. 9 shows a diagram of the energy levels of the nitrogen molecule as computed from spectroscopic data by Birge and Hopfield.‡ The position of the triplet levels with respect to the ground level of the molecule is subject

* ‘Trans. Faraday Soc.’ vol. 23, p. 552 (1927).

† ‘Z. Physik,’ vol. 18, p. 304 (1923).

‡ ‘Astrophys. J.’ vol. 68, p. 257 (1928).

to the uncertainty of 0.3 volts in the experimental determination* of the smallest potential difference necessary for the excitation of the first lines of

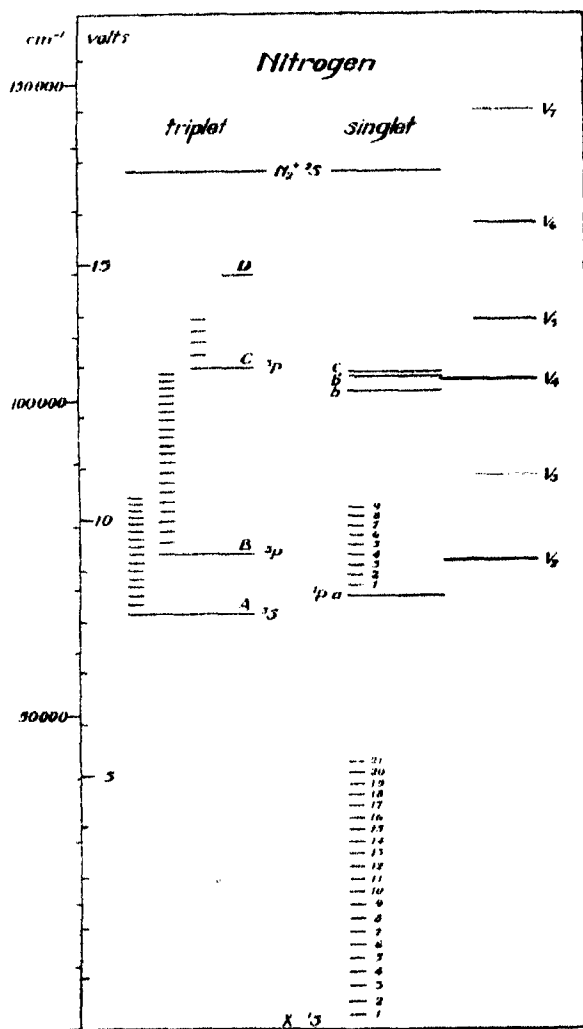


FIG. 9.

the second positive group (level C). The level at the top of the diagram, denoted $N_2^+ \ ^2S$, indicates the ionisation potential of the molecule as determined by electrical methods.

The lowest level for the molecule, X, corresponds to a singlet state. No transitions between this and the triplet states are evident from the spectrum,

* Sponer, 'Z. Physik,' vol. 34, p. 622 (1925).

either in absorption or emission. Transitions from the X-level to the singlet state a have been found in absorption by Sponer* and by Birge and Hopfield (*loc. cit.*); transitions involving the other singlet states have only been obtained in emission. It is natural to expect† that the action of a bombarding electron on the nitrogen molecule resembles that of a radiation quantum at least in the one respect that the resulting transition would preferably be to a singlet state.‡ One would, therefore, expect the measured energy losses of the colliding electrons to correspond, in the first instance, to the term values for the different singlet states of the molecule, unless the energy loss exceeds the ionisation potential. The positions of the maxima in the distribution curves measured in the present investigation have been marked off to the right in fig. 9. It will be seen that the strongest peak V_4 is in excellent agreement with the position of the three singlet levels b, b', c , according to Birge and Hopfield. The spectroscopically determined term values for these levels are included in Table III. A separation of the contributions to the peak by the different levels is practically excluded with the present resolving power of the method.

The maximum V_2 falls a good deal above the lowest a -level. In fact it comes fairly near to the first B-level of the triplet system. It would seem better, however, to adhere to the view that transitions to the singlet states are the ones which generally should occur, and therefore try to identify V_2 with the a -state. For this purpose it is necessary to consider what is the most probable transition to the a state from the lowest level of vibrational number 0 for the X state, which should be the one in which a colliding electron is likely to find the nitrogen molecule at ordinary temperatures. Unfortunately there are no data available for the relative intensity of these bands in absorption. I have therefore made an attempt to estimate the transition of maximum probability, based on the theory of transition probabilities by Franck§ and Condon,|| using the experimental data published by Birge and Hopfield for the intensities of the a -X bands in emission. The curves to the left in fig. 10 show the relative intensities of the bands due to transitions from the first five vibrational levels $v' = 0 - 4$ of the a state, as plotted from the table by Birge and Hopfield. As remarked by these authors, the intensity distribution

* 'Proc. Nat. Acad. Sci.,' vol. 13, p. 100 (1927); 'Z. Physik,' vol. 41, p. 611 (1927).

† Bethe, 'Ann. Physik,' vol. 5, p. 325 (1930).

‡ This was verified experimentally for the similar case of collisions in helium by Dymond and Watson, 'Proc. Roy. Soc.,' A, vol. 122, p. 571 (1929).

§ 'Trans. Faraday Soc.,' vol. 21, p. 536 (1925).

|| 'Phys. Rev.,' vol. 28, p. 1182 (1926).

in the case of the higher vibrational levels exhibits certain irregularities, which are not provided for by the simple theory. Disregarding these for the present,

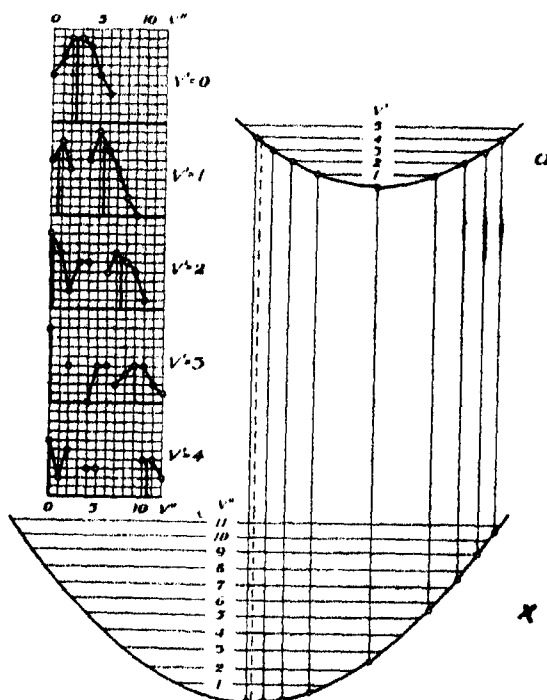


FIG. 10.

I find that the main maxima in the distributions occur in the positions indicated by heavy vertical lines in the diagram. The rotational structure of these bands has not been investigated, and therefore the curve for the potential energy as a function of the nuclear separation is not known for any of the two states involved. Under these circumstances I have made the simplest assumption which appeared reasonable, *viz.*, that for the present purpose this curve may be represented to a sufficient approximation by a parabola in the case of the first vibrational levels for the X-state. The positions of the maxima in the intensity distribution would then, by the Franck-Condon theory, yield the potential energy curve for the *a* state which is indicated to the right in fig. 10. From the position of this curve with respect to the corresponding graph for the X-state it may be inferred that the most probable transitions from the deepest X-level will be those going to the levels $v' = 3$ and $v' = 4$ of the *a*-state. As regards the question how far this result depends on the some-

what arbitrary shape assumed for the potential energy function of the X-state, it is evident that if the positions of the left-hand maxima in the intensity distributions were accurately known from the intensities alone the same result could have been obtained directly, no reference to the potential energy curves being necessary. Owing to the irregularities in the vicinity of the left-hand maxima for higher v' values, however, I have used the symmetrical potential energy curve determined by the better defined right-hand maxima to locate, with better accuracy, the maxima near $v'' = 0$. The values so obtained check with the experimentally determined distribution of intensity. It should perhaps be repeated that since the Franck-Condon theory leads to a qualitative, rather than a quantitative rule, the results obtained can only be expected to be of an approximate validity, even in cases for which the potential energy functions are accurately known.*

The conclusion arrived at from the above considerations, that the most probable transitions from the non-vibrating X-state to the α -state should involve the excitation of vibrations of quantum numbers 3 and 4 in the latter state, fits very well with the position of the maximum V_2 , as may be seen in fig. 9 and from Table III. The considerable width of this maximum compared with the primary peak, and also with the peak V_4 , may well indicate that there is a comparatively high probability for the excitation of the nearest vibrational levels in addition to these two, a result consistent with the intensity data for the emission bands. The rather wide spread of the critical potential values for this region is very likely due to the same cause. It is reasonable to expect that the singularity recorded as the critical potential in such experiments may correspond to the lowest α -state, the region of maximum intensity or perhaps some intermediate point, depending on the particular method adopted. By the original picture of molecular transitions from which the Franck-Condon theory was developed, one might possibly think that collisions

* [Note added in proof.—There is a second way of obtaining the shape and relative positions of the potential energy curves without making use of any intensity estimates. Morse ('Phys. Rev.', vol. 34, p. 57, 1929) has given a general formula for the potential energy of a diatomic molecule as a function of the nuclear separation and has further shown that certain empirical relations exist, which enable the characteristic constants of this function to be estimated from vibrational data alone. Using the constants computed by Morse, I have drawn the curves and marked off the vibrational levels, taking account of the zero point energy for $v = 0$ according to the new mechanics. The range of possible nuclear separations in the initial state corresponds to $v' = 1 - 6$ for the α -state and a value $v' = 2$ in the case of the equilibrium position (of maximum intensity). The difference is entirely of the order of magnitude to be expected in view of the uncertainty in the constants deduced from Morse's empirical relations, which are only approximately valid].

by fast electrons should conform better to the predictions of the theory than collisions in which almost all the energy of the electron is spent. It is not at all certain, however, that one is justified in pursuing the simple mechanical picture of the transition process to such details as this. There is no obvious trend in the V_2 values of Table I as the bombarding voltage is increased, and this should not be expected, since the energy loss is only a small fraction of the total energy in all cases.

The other maxima found in the energy loss curves, of which at least V_5 and V_6 should be attributed to nitrogen, have not been correlated with any known spectroscopic levels at present. It seems possible that levels corresponding to these maxima could be involved in the transitions which give rise to some of the many remaining lines on the plates obtained by Birge and Hopfield, which have not as yet been classified.

It is remarkable that no maximum corresponding to the first ionisation potential has been found in the distribution curves. The energy loss V_6 is a good deal too low to permit of the interpretation that N_2^+ ions are generated, when this amount of energy is imparted to the normal molecule. It seems rather likely, however, that the continuous distribution which has been found to extend for some distance to the side of greater losses from V_6 results from collisions involving such single ionisation of the molecule. The continuous background in the region of the other maxima must be attributed to scattering at the electrodes, but the blank experiments show that this background becomes too small in the region of higher losses to account for the continuous distribution in this region when nitrogen is present. Adopting the view that this part of the curve is due chiefly to ionisation of the molecule, the results must be taken to show that the kinetic energy with which the emitted secondary electron escapes is mostly different from zero and is distributed over a considerable range of values in such a way that no sharp rise is produced at the ionisation potential in the energy loss curves. The total absence of any rise whatever in this region would seem to require that the maximum V_6 must extend so far to the side of higher losses that any rise, otherwise present, is completely masked by overlapping of the decreasing V_6 -curve. On this view the most natural interpretation of the very broad maximum V_7 , which has only been recorded as a maximum in a small number of the experiments, is perhaps to say that ionisation processes with a surplus energy of about 1.1 volts imparted to the secondary electron seem to be slightly more favoured than others.

Absence of Energy Losses due to K-Ionisation.

Several experiments were carried out in which the full region of velocities of the scattered electrons from zero to the value corresponding to the bombarding voltage was investigated, with the object of looking for evidence of ionisation processes pertaining to the K-level. In these measurements the electrode B was directly connected to the deflection box and slit S_1 , and the voltage across the plates was varied by small amounts. It has been mentioned that Mohler and Foote (*loc. cit.*), from critical potential experiments, concluded that the K-ionisation potential of molecular nitrogen is 374 volts. Holweck* obtained a value 397 volts in absorption measurements, using soft X-rays; recently Thibaud† and Söderman‡ have measured the K_α -line of nitrogen, recorded by the vacuum spectrograph, with the result $K_\alpha = 388$ and 388.6 volts, respectively. Hence the ionisation of the nitrogen K-level should give rise to a maximum in the distribution curves corresponding to a loss somewhere in the region 370–410 volts. The bombarding voltages used in these experiments were therefore chosen well above 400 volts. The highest bombarding voltage employed was 587 volts. With voltages of this magnitude the maxima which have been found to group themselves round the prominent peak V_4 are not as a rule resolved, and no attempt has been made to improve the accuracy in this region. A typical example of the curves obtained is shown in fig. 11. It is at once evident from this curve that there is no sign of a characteristic energy loss in the region in question. The other curves that have been measured show the same perfectly smooth appearance in the neighbourhood of 400 volts' loss. The sensitiveness of the test offered by the measurements in fig. 11 is perhaps better judged from the following data, which refer to the same curve. For the region in question, the total current received by the collector produced a steady deflection of the electrometer amounting to about 3 mm. of the scale. A maximum of 2 mm. could not possibly have escaped detection. If these figures are to be compared with the corresponding values for the full velocity electrons, they should be multiplied by a factor about 4 in order to refer to the same effective width of the analyser. The $V_{4,6}$ maximum, however, which will be seen to the left in fig. 11, was 9.5 metres on the same scale, and the primary peak 148 metres!

It will be remembered that the experimental arrangements used in the

* 'C. R.,' vol. 182, p. 779 (1926).

† 'C. R.,' vol. 185, p. 642 (1927).

‡ 'Z. Physik,' vol. 52, p. 795 (1929).

present work are such that only practically undeflected electrons are able to contribute to the distribution curves measured. It might, therefore, be

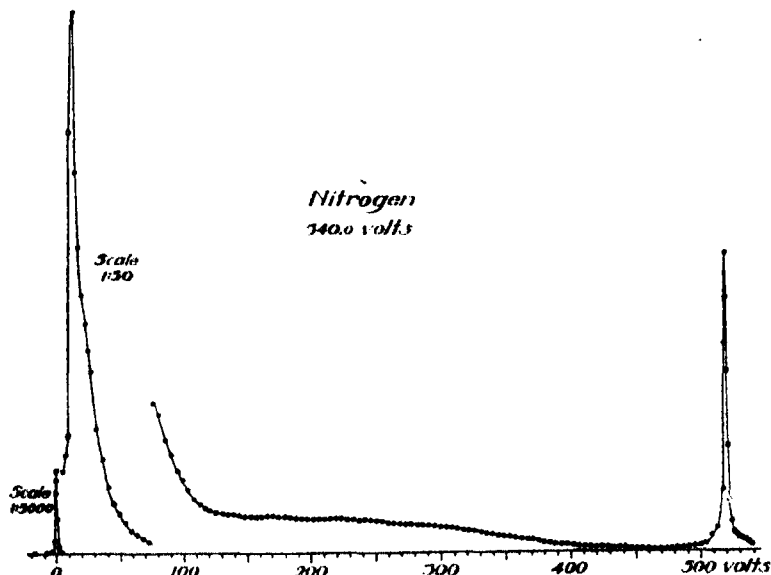


FIG. 11.

suggested that the failure of these experiments to reveal any features, attributable to K-ionisation processes, could be due to the fact that the chance for a colliding electron to continue in the same direction after the event was very small in the case of such processes, notably when the energy lost is a large fraction of the total energy. Although both theory and experiment show that the angular distribution after collision depends to a certain extent on the particular atomic or molecular transition excited, there is, so far as I am aware, no case hitherto found or predicted with such a minimum in the angular distribution for zero angle of deflection, as would be required if this explanation is the correct one. On the contrary, the distributions so far studied exhibit a maximum* for zero deflection and theoretical considerations† require that this maximum should be even more pronounced in the case of inelastic collisions than for elastic scattering. It is true, however, that the present theories of such processes lead to the result that the kinetic

* Harnwell, 'Phys. Rev.', vol. 33, p. 559 (1929); *ibid.*, vol. 34, p. 661 (1929); Dymond and Watson, 'Proc. Roy. Soc.,' A, vol. 122, p. 571 (1929); Arnot, *ibid.*, vol. 125, p. 660 (1929); Whiddington and Jones, 'Phil. Mag.', vol. 6, p. 889 (1928).

† Bethe, 'Ann. Physik,' vol. 5, p. 325 (1930).

energy transferred to the escaping secondary electron should often be quite considerable for levels of a high ionisation potential. It should therefore be possible for the energy imparted to the escaping K-electron to be uniformly distributed over such a wide range of values, that no sharp rise to a maximum at the ionisation potential can result in the curves for the energy loss. Even if this is the case, however, I believe that the present experiments must be taken to show, that the probability for the colliding electron to produce the emission of a K-electron is very small, compared with that of displacing an outer electron, for the range of primary velocities which has been studied in this investigation. It should be remarked that this result, bearing on the relative probability of different types of inelastic collisions in a gas, is qualitatively the same as the result for the corresponding probabilities in the case of bombarded solids, which has previously been investigated by the present writer.*

Summary.

The velocity distribution of an initially homogeneous beam of electrons has been determined after passing through a chamber containing nitrogen at a pressure of the order 0.01 mm. The method of velocity analysis adopted is based on a special type of electrostatic deflection, which combines the advantage of considerable resolution with a valuable focussing property, when slightly divergent beams are used.

Seven maxima have been measured in the distribution curves in the region corresponding to individual energies 0-30 volts less than the primary voltage. These indicate characteristic energy losses suffered by the primary electrons in collisions. The smallest loss measured is attributed to collisions with the electrodes. The strongest maximum observed, which in addition is rather sharp, indicates a loss of 12.78 volts. This and one further prominent maximum are interpreted as due to excitation of the first singlet levels of the nitrogen molecule, known from far ultra-violet spectra. Two further definite maxima are probably related to similar levels; the corresponding spectra have not been classified at present.

A search for a characteristic energy loss connected with the ionisation of the nitrogen K-level has given negative results. This test was a rather sensitive one. It is concluded, that the probability of ionisation in the K-level is very small in comparison to the probability for excitation of an outer level for the bombarding voltages studied (about 600 volts).

* 'Kungl. Svenska Vet. Akad. Handl.,' vol. 7, No.1 (1929).

On a Search for Radiation accompanying the Scattering of Comparatively Slow Electrons at the Surface of Incandescent Solids.

By ERIK RUDBERG, Nobel Institute, Stockholm, Sweden.

(Communicated by O. W. Richardson, F.R.S.—Received July 21, 1930.)

In an earlier* paper published in these 'Proceedings,' I gave a report of some measurements of the energy losses suffered by electrons scattered from incandescent solids. The substances tested were copper, silver, gold, platinum and the oxides of magnesium, calcium, strontium and barium. In every case the energy distribution curves for the electrons after scattering were found to exhibit characteristic maxima, different for different substances. The energy loss by the scattered electrons, indicated by the position of any particular maximum, remained the same as the initial energy of the bombarding electrons was varied within wide limits. This fact, together with other evidence, led to the conclusion that the corresponding scattering processes must involve the excitation of definite energy levels pertaining to and characteristic of the scattering substance. Particularly the three last-mentioned oxides were found to yield several rather definite and persistent maxima. The present conceptions as regards the mechanism of light emission would make one expect such emission to occur as a result of, or in connection with, the return of the disturbed scattering system to its normal state, the frequency of the radiation being related to the characteristic energy values concerned by the Bohr relation. As pointed out in the previous report, however, existing experimental data by different investigators fail to show any evidence of this radiation for bombarding voltages of the order 0–1000 volts, at any rate in the case of metals.†

In view of the importance of establishing the true nature of these energy levels, I have made a fresh attempt to look for radiation from solid substances bombarded with electrons of velocities of the same order as was used in the scattering experiments referred to. For certain reasons I had to confine the investigation to the region of the visible and the ultra-violet above 2300 Å., which is accessible by a quartz spectrograph. However, some of the characteristic losses previously observed were small enough to correspond to this region,

* 'Proc. Roy. Soc.,' A, vol. 127, p. 111 (1930).

† Compare also Rudberg, 'K. Svenska Vet. Akad. Handl.,' vol. 7, No. 1, p. 98 (1929).

and transitions in which a pair of the measured energy values were concerned should often yield frequencies in the range studied. The chief difference of the present investigation from earlier work by others, rests in the fact that the bombarded substances are maintained at incandescence during the whole time of exposure. This method was adopted since the electron scattering experiments had shown, that allowing the target to cool down often caused the characteristic maxima to diminish and gradually disappear, the distribution curve being replaced by a new one, the same for all kinds of targets.* The details of this change were such as to suggest that an adsorbed film of some substance, present as a vapour of low pressure in the tube in spite of the high vacuum, was slowly formed on the surface of the target and that this film, once formed, was largely responsible for the scattering of electrons with small energy losses observed with cold targets. To enable heating of the substance under investigation this was therefore deposited on a strip of thin platinum foil, which could be heated by the passage of an electric current from a battery of accumulators. However, the dissipation of heat from the bombarded area of the long strip was so slow that with the heavy bombarding currents used the foil was often maintained at incandescence by the discharge alone.

A diagram of the tube is shown in fig. 1. It is made of glass, but the inside wall of the central part is kept at a well-defined potential by the aid of a lining of sheet copper S connected to the hot cathode C. The upper lead to the cathode strip is constructed as a shield preventing direct light from the cathode reaching the spectrograph. When the oxides of calcium, strontium and barium were bombarded, the same oxide which was used for the anode formed the dull-emitting deposit of the cathode. In the experiments with metal targets a mixture of strontium and barium oxide was mostly employed. A quartz lens serves to focus the light emerging from the anode A through the fluoride window on to the slit of the quartz spectrograph (a small Leiss monochromator fitted with a camera). The visible region was investigated directly using a larger glass spectrometer. Baking of the central parts of the tube in an electric furnace at 400°C. each time after assembly, and continuous bombardment with the pumps running, helped to establish a high vacuum during the exposures, generally characterised by a tendency for the mercury of the McLeod to stick in the capillary. The trap for mercury vapour was cooled with carbon dioxide and acetone.

Several plates were taken with anodes of calcium, strontium and barium oxide and the metals copper and silver—the latter ones in the shape of thin

* 'K. Svenska Vet. Akad. Handl.,' vol. 7, No. 1, p. 120 (1929).

pieces of foil attached to a strip of platinum. The bombarding voltage was about 600 volts and the current of the order 5 milliamps. The exposures

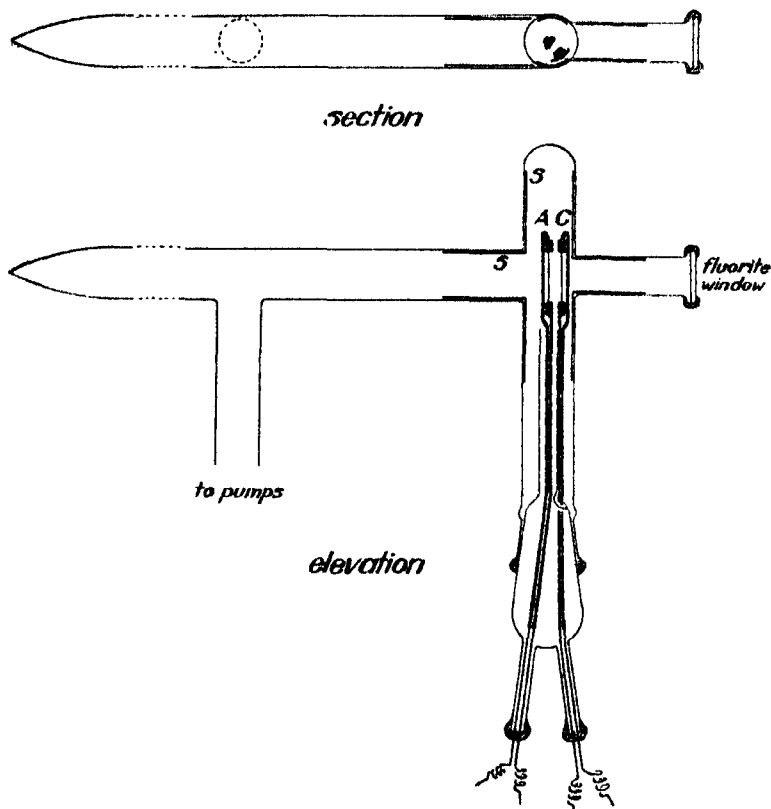


FIG. 1.

varied from 2 to 24 hours. Wave-lengths were determined by the aid of a series of spectra from an iron arc in air and from a mercury lamp (for orientation) recorded on each plate.

Even in the case of the longest exposures the photographic impressions obtained were rather weak. All the plates, however, show the same type of spectrum. This consists of most of the stronger lines present in the spectrum of the mercury arc and a number of bands, mostly very faint. The latter ones have been identified with the ultra-violet band spectrum of the OH molecule.* The different spectrograms secured exhibit a greater or smaller number of the strongest band lines of this spectrum, according to the time of

* Eder, 'Denkschr. Akad. Wiss. Wien.,' math.-nat. kl., vol. 57, p. 531 (1890); Jack, 'Proc. Roy. Soc.,' A, vol. 115, p. 373 (1927).

exposure, but the relative intensities remain the same. The most prominent water vapour band at 3064 Å., together with the mercury resonance line, gives the strongest blackening of the plates. No other lines or bands could be detected, although I have not attempted to identify as OH lines a few extremely weak and uncertain impressions found in a few single cases. The OH spectrum is believed to originate in the space between the electrodes, although the concentration of the molecules must have been very small. This spectrum has been found to persist in discharge tubes filled with pure oxygen even after very intense drying. Its presence under these conditions, which at one time was taken to prove that the spectrum was due to oxygen, is accounted for by the evolution of hydrogen in small amounts from the electrodes in the tube. In the present experiments the pressure of oxygen due to decomposition of the heated oxides must have been vanishingly small. The same must be true of the pressure of mercury vapour, which in spite of the cooled traps was sufficient to give rise to the characteristic spectrum of this element with the long exposures that were employed. The very low yield of radiant energy in this region may be estimated from the fact that, to bring out perfectly the comparison spectrum of the mercury arc (150 volts, 2.5 amps.) placed in the same position as the anode relatively to the slit, 1/10 second was amply sufficient. The input over the region from which the spectrograph is receiving radiation, I have estimated to be 3 watts in the vacuum tube, and less than 10 watts in the mercury arc, being thus of about the same order of magnitude. The ratio of the light intensities is certainly less than 10^{-6} , which figure from the above consideration should also illustrate the efficiency of light production in the vacuum tube compared with the mercury arc. In the region here considered any radiation produced in the scattering process at the anode surface must be of an efficiency a good deal smaller than this.

In the visual observations of the spectrum from the tube no lines or bands could be detected. This result is necessarily of a more restricted character, since the light from the dull-emitting cathode and that due to the temperature of the anode itself must mask any weak effects in this region. On the other hand several of the plates showed no fog even at 4300 Å.

The result of this investigation is thus, that there is no appreciable radiation emitted in the visible and the ordinary ultra-violet under the conditions for which the characteristic energy losses by scattered electrons have been found to occur. The spectral region beyond the ultra-violet frequency limit, where the quartz ceases to be transparent, has not been investigated, so that the statement does not immediately apply to such radiation. Since, however,

the same negative result was obtained with a number of different target substances for which rather different energy losses of electron scattering have been found, and since the higher energy losses are in no other respect distinguished from the low ones, which would correspond to frequencies in the region here studied—it seems extremely likely that, quite generally, the re-arrangement of the disturbed system after such an inelastic scattering process takes place without emission of radiation.

Gaseous Combustion in Electric Discharges. Part VI.—The Effect of Diluents upon the Cathodic Combustion of Carbonic Oxide "Detonating Gas."*

By G. I. FINCH and W. L. PATRICK, Imperial College of Science.

(Communicated by W. A. Bone, F.R.S.—Received July 14, 1930.)

Introduction.

A spectrographic examination of the cathodic combustion of carbonic oxide "detonating gas"† has shown that carbonic oxide ions are not formed in either the cathode or interelectrode zones under the conditions of our experiments (V). This fact proves that carbonic oxide molecules can be burnt cathodically without being ionised. The observed acceleration of the rate of cathodic combustion of "detonating gas" by steam and/or metal particles cannot, therefore, be attributed to the overcoming of the electrostatic forces of repulsion existing between similarly charged ions (III and IV).

The present investigation was originally undertaken with the object of submitting certain of our earlier views to the test of experiment. During its prosecution, however, Prof. S. Chapman, F.R.S., suggested to us that considerations arising out of the three-body collision theory might lead to a satisfactory explanation of the mechanism of the combustion of "detonating gas"; and since then the investigation has been considerably extended in order to

* 'Proc. Roy. Soc.,' A, vol. 111, p. 257 (1926) (Part I); vol. 116, p. 529 (1927) (Part II) vol. 124, p. 303 (1929) (Part III); vol. 125, p. 352 (1929) (Part IV); vol. 129, p. 314 (1930) (Part V); these will be referred to by their Roman numerals in brackets.

† For brevity a mixture of carbonic oxide and oxygen in their combining proportions will be referred to herein as "detonating gas."

enquire more closely into the precise nature of the rôle or rôles played by such promoters of cathodic combustion as metal atoms and steam molecules.

Experimental.

The experiments were carried out in the circulation apparatus previously described in (III), in which and in (IV) the experimental procedure now followed has also been set forth.

Gold and tantalum electrodes, which had served for the purpose of the experiments previously described in (III) and (IV), and silver electrodes were employed. The gap width, current and pressure ranges chosen were such as to exclude positive column combustion, without at the same time giving rise to distortion of the cathode glow through the use of too narrow a gap width.

The mixtures of "detonating gas" and the various diluents employed were stored in steel gas-holders over mercury, the exact proportions being checked after mixing by analyses carried out in a "Bone-Newitt" gas analysis apparatus.

Since the products of combustion were continually removed, the concentration of any diluent gas increased as the total pressure fell.

The Experimental Results.

In all, 16 series of experiments were carried out, the gases employed to dilute the "detonating gas" being nitrogen, helium, argon, carbonic oxide and oxygen. In the two final series the auto-oxidation of pure dry carbonic oxide was studied.

Series I to VIII.—The diluents were nitrogen, helium and argon. The mixture was dried by passage over redistilled phosphoric oxide contained in a 60-cm. long tube in the circulation system. A gold cathode was employed. The current was kept constant throughout each experiment, three to five experiments being carried out in each series. Further data are summarised in Table I.

From the known volume of the apparatus and the fall in pressure-time curves constructed from the manometer readings* taken at suitable intervals, the values of c/i (cubic centimetres of "detonating gas" at N.T.P. burnt per minute to the current in milliamperes) for the different percentage concentrations of diluent gas were obtained. The results are shown in fig. 1

* Mean values, because the mercury level rose and fell through a narrow range with each stroke of the circulation pump.

Table I.

Series.	Initial composition of the mixture.	Initial total gaseous pressure in mm.	Limits of current range in milliamperes.	Gap width in mm.
I	$2\text{CO} + \text{O}_2 + \text{N}_2$	90	} 3.65 to 4.38	1.2 to 1.4
II	$2\text{CO} + \text{O}_2 + \text{N}_2$	120		
III	$2\text{CO} + \text{O}_2 + 3.78\text{N}_2$	90		
IV	$2\text{CO} + \text{O}_2 + 3.78\text{N}_2$	120		
V	$2\text{CO} + \text{O}_2 + \text{He}$	90	} 3.25 to 4.38	1.4
VI	$2\text{CO} + \text{O}_2 + \text{He}$	120		
VII	$2\text{CO} + \text{O}_2 + \text{A}$	90	} 3.25 to 4.38	1.3
VIII	$2\text{CO} + \text{O}_2 + \text{A}$	120		

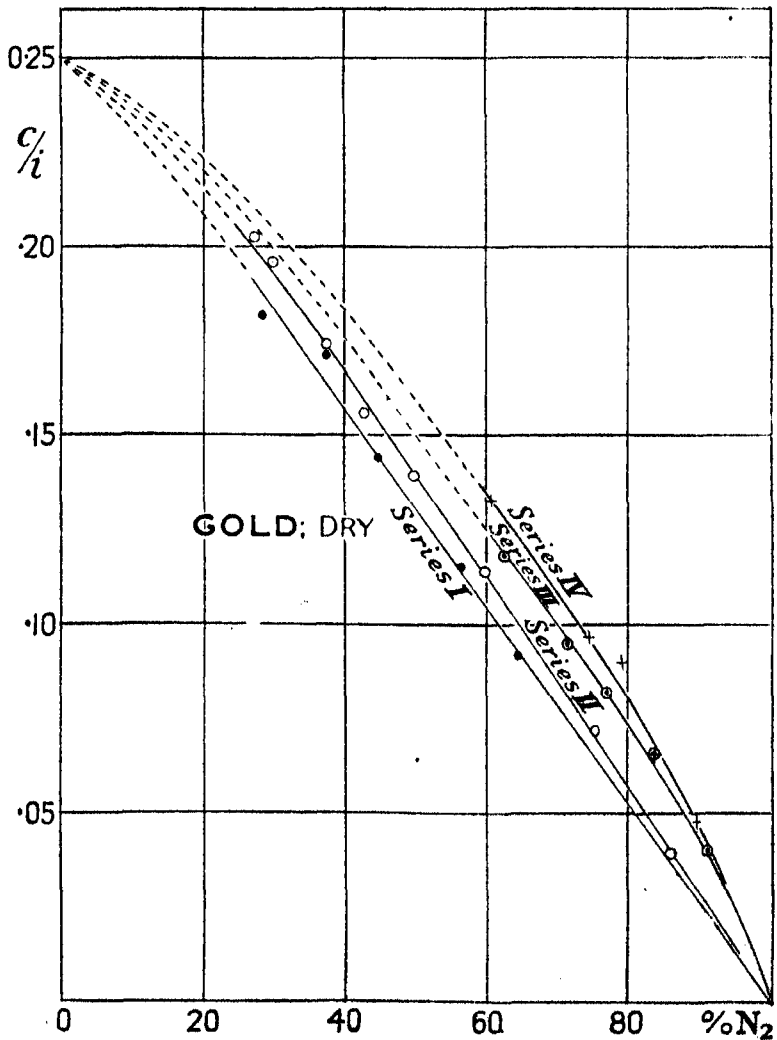


FIG. 1.—Cathodic Combustion of dry $2\text{CO} + \text{O}_2$ diluted with N_2 .

(nitrogen) and fig. 2 (helium and argon). The values of c/i for the undiluted "detonating gas" are taken from Part III.

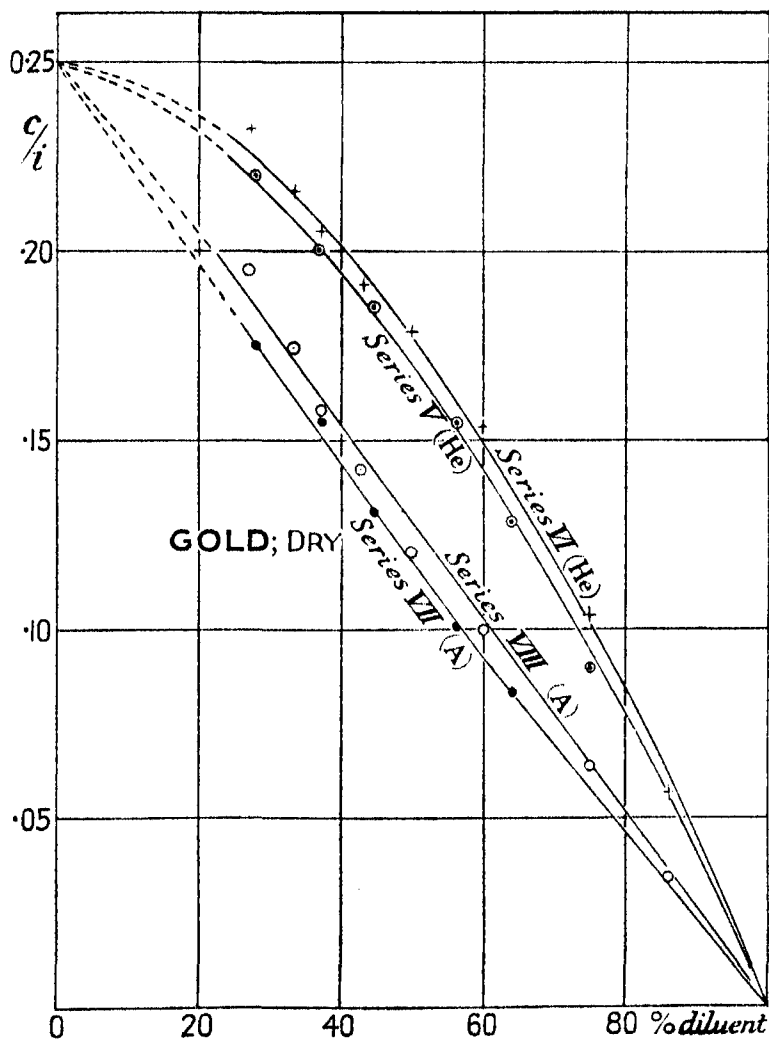


FIG. 2.—Cathodic Combustion of dry $2\text{CO} + \text{O}_2$ diluted with He or A.

Series IX.—In this series was studied the cathodic combustion at a gold, *i.e.*, freely sputtering, electrode, of mixtures of carbonic oxide and oxygen in varying proportions and dried by circulation over redistilled phosphoric oxide contained in a 60-cm. long tube. The initial composition and total gaseous pressures of the different mixtures at the beginning of each experiment were as follows:— $2\text{CO} + \text{O}_2 + \text{CO}$ (120 and 90 mm.); $2\text{CO} + \text{O}_2 + \text{O}_2$ (140, 130, 120 and so

on down to 50 mm.); $2\text{CO} + \text{O}_2 + 2\text{O}_2$ (120, 90 and 60 mm.). The current range was between 2.92 and 4.38 milliamperes, and the gap width between 0.9 and 1.0 mm. The results are recorded in fig. 3. Since the total pressure at any one stage of combustion for any given percentage concentration of diluent was proportional to the initial pressure of the mixture, the experimental results would give points lying on the same smoothed curve only in

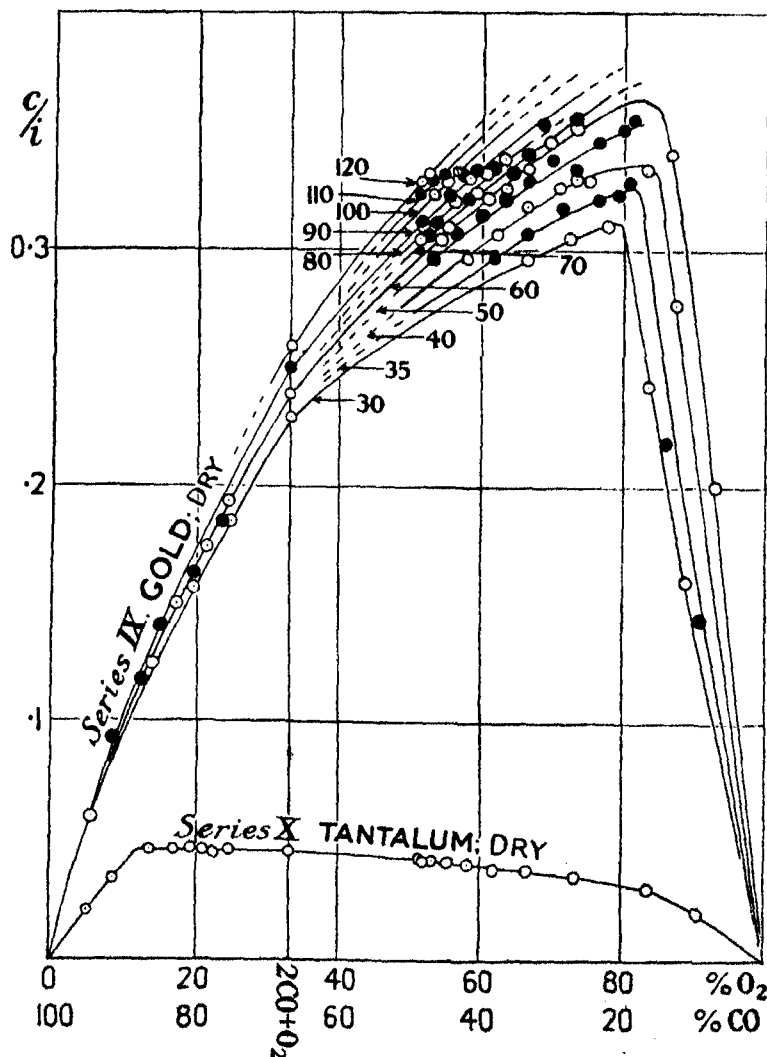


FIG. 3.—Cathodic Combustion of dry $\text{CO} + \text{O}_2$ mixtures. The numbers assigned to the curves denote total pressures in millimetres. To avoid confusion points belonging to alternate curves in series X are indicated by dots and circles respectively.

the event of the value of c/i being throughout independent of the pressure. The results show, however, that, for any given excess of diluent, c/i increases with the total pressure, the effect being more pronounced the greater the excess of oxygen. The values of c/i for the undiluted "detonating gas" incorporated in fig. 3 have been taken from Part III.

Series X.—This series was carried out with a tantalum, *i.e.*, non-sputtering cathode; otherwise the experimental conditions were similar to those of Series IX, the mixtures being dried as before over phosphoric oxide. The results are recorded in fig. 3, curve tantalum. It will be noted that the value of c/i is, within the limits of experimental error, independent of the total gaseous pressure.

Series XI.—In the case of this series the experimental conditions differed from those of Series X (dry, non-sputtering cathode) only in that the gaseous mixture, instead of being dry, was moist, the partial pressure of steam being maintained constant throughout the series at 3 mm. by means of a tube, containing suitably diluted sulphuric acid, incorporated in the circulation system in place of the phosphoric oxide tube. The results are recorded in fig. 4.

Series XII.—The experimental conditions were similar to those of Series IX except that the mixture contained 3 mm. partial pressure of steam. The results are recorded in fig. 5. The values of c/i for the undiluted "detonating gas" in figs. 4 and 5 are taken from Parts III and IV.

Series XIII and XIV.—In these two series the experiments of Series IX and XII were repeated, but with a silver cathode. The results are similar to those of Series IX and XII, and will be incorporated in two figures in the next communication of this series.

At an early stage in the course of this investigation, hydrogen peroxide had been detected in the cathodic combustion products of moist "detonating gas," and in several of the experiments of Series XI and XII the amount of hydrogen peroxide formed was estimated quantitatively. For this purpose a known volume of a standardised acid titanous sulphate solution was placed in a horizontally disposed tube, 10 cm. long, inserted in the circulation system immediately after the combustion vessel. Thus, after passing through the discharge, the moist mixture, the composition of which at the initial pressure of 120 mm. had corresponded to $2\text{CO} + \text{O}_2 + \frac{1}{2}\text{O}_2$, was circulated over the surface of the titanous sulphate solution. The partial pressure of moisture in the "detonating gas" mixture was 3 mm. Each experiment was continued until the pressure had fallen to 30 mm., whereupon, after filling the

circulation system with air to atmospheric pressure, the titanous sulphate tube was cut out and its contents compared colorimetrically with standards made

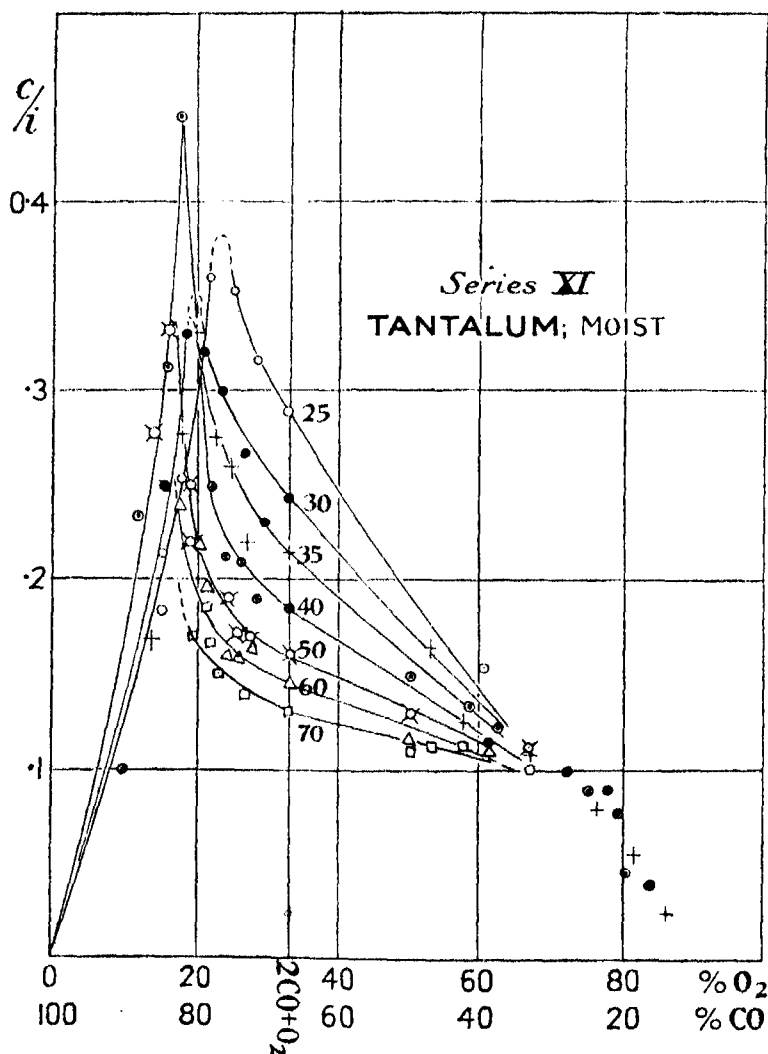


FIG. 4.—Cathodic Combustion of moist $\text{CO} + \text{O}_2$ mixtures. The numbers assigned to the curves denote total pressures in millimetres.

up with known amounts of hydrogen peroxide. It was found that, when a moist gaseous mixture of the composition stated above was burnt at a tantalum cathode, 0.06 per cent. of the oxygen originally present in the mixture was recovered in this manner as peroxide oxygen; at a gold cathode the corresponding amount was only 0.02 per cent.

We also found in some of the later experiments of this series that, when moist "detonating gas" containing 2 mm. partial pressure of steam was burnt

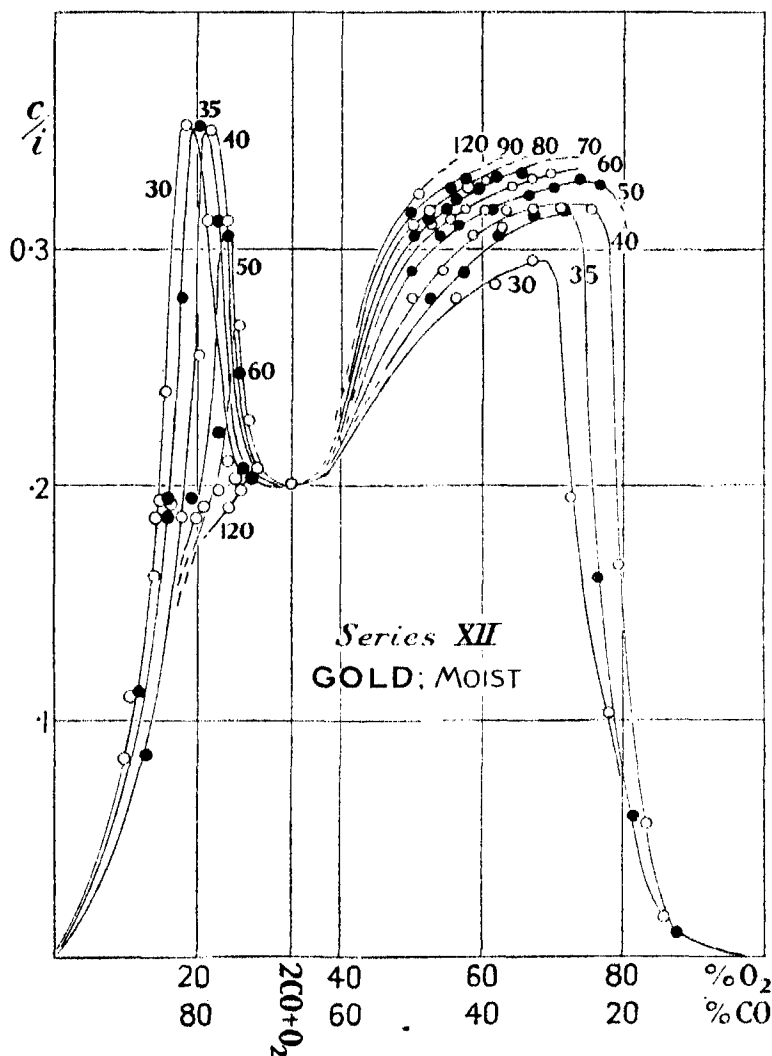


FIG. 5.—Cathodic Combustion of moist $\text{CO} + \text{O}_2$ mixtures. The numbers assigned to the curves denote total pressures in millimetres.

cathodically until the initial total pressure had fallen from 120 mm. to a final pressure of 30 mm., the final mixture contained hydrogen and that the amount thereof was greater when combustion had been effected at a sputtering (silver) cathode than when a non-sputtering (tantalum) electrode had been employed.

Series XV and XVI.—The deposition of a thin film of carbon on the cathode

had been observed during the combustion of mixtures of dry "detonating gas" diluted with carbonic oxide. In order to follow up this observation the present two series of experiments were carried out with tantalum (Series XV) and gold cathodes (Series XVI).

Pure dry carbonic oxide was circulated through the discharge, any carbon dioxide formed being subsequently absorbed. Current and gap width were suitably adjusted in order to confine combustion to the cathode zone. Experiments were carried out with gap widths of 1 and 2.5 mm. Carbon deposition on the cathode gave rise to trouble with the narrower gap width owing to distortion of the cathode glow followed by bridging and short circuiting of the gap. The initial gaseous pressures were 100 and 30 mm. respectively. The results are set forth in Table II.

Table II.— c/i Values for the Cathodic Auto-oxidation of Carbonic Oxide.

Initial gaseous pressure in mm.	Series XV tantalum cathode.	Series XVI gold cathode.
100	0.010	0.008
30	0.013	0.012

It should be pointed out that, owing to possible experimental error, it would not be safe to infer from these results that the rate of auto-oxidation of carbonic oxide increases with decreasing pressure. The weights of carbon deposited on the cathodes in these experiments were such as to account for practically the whole of the carbon formed during the reaction.

Discussion of the Results.

The experimental results of Series XV and XVI prove that carbonic oxide is slowly burnt in the cathode zone to carbon dioxide with deposition of carbon upon the cathode surface. Either CO is directly oxidised by CO, or CO is first dissociated into carbon and oxygen, which latter then oxidises the carbonic oxide. The fact, however, that in the experiments set forth in (V) the "CO" band, but not the "Swan," spectrum was obtained in pure CO, enables the conclusion to be drawn that, under the conditions of our experiments, CO is directly burnt by CO. The equilibrium in the reversible system $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$

has been studied by Rhead and Wheeler* who found that it shifts from right to left with increasing temperature, and that in the equilibrium mixture at 1200° C., the maximum temperature employed by them, the percentages of CO₂ and CO were 0.06 and 99.94 respectively. But the fact that the "CO" band spectrum was obtained by us far up into the ultra-violet (V) proves conclusively that the internal energy of the CO molecules within the cathode zone must correspond to a far higher, and therefore even more unfavourable, temperature from the point of view of the CO₂ concentration. That, in spite of this, auto-oxidation proceeds at such a comparatively high rate as that recorded above must therefore be due to the equilibrium mixture being continually and rapidly disturbed. Carbon, a product on the right-hand side of the reversible system, is, in fact, as has been shown above, deposited quantitatively on the cathode surface, and is thereby completely removed from the sphere of reaction in the cathode zone, within which all changes and reactions taking place are homogeneous; because the ratio of the rate of combustion to current is a constant for any given set of conditions wherein the current, and hence also the area of the cathode enclosed by the cathode zone, alone is changed.

The fact that the rate of auto-oxidation of CO is only between a quarter to a third of that of the cathodic combustion of dry "detonating gas" might be wholly accounted for on the supposition that the oxygen present in the latter mixture removes the carbon formed during CO auto-oxidation so much more rapidly by oxidation than would occur otherwise under the influence of drift to the cathode alone. The remarkable effect of sputtered metal particles, however, in promoting the cathodic combustion of dry CO — O₂ mixtures suggests that, in addition to combustion resulting from the auto-oxidation of CO with subsequent oxidation of carbon by oxygen, CO may also be burnt directly by oxygen at a non-sputtering cathode.

Born and Franck† have discussed the conditions under which two uncharged atoms or molecules, A and B, can combine to form a single molecule, AB, which may be either polar or non-polar. They have shown that if AB be formed and is to continue to exist as a stable molecule in the absence of a third body at the moment of collision of A and B, then the energy of AB on formation must be exactly quantised, because the mean centre of gravity of the system moves along the same straight path with unimpaired velocity

* 'Trans. Chem. Soc.,' vol. 101, pp. 101 and 946 (1912); vol. 103, pp. 103 and 461 (1913).

† 'Ann. d. Phys.,' vol. 76, p. 225 (1925).

before, during and after collision. This condition can be but extremely rarely fulfilled, because the total energy associated with AB on formation, consisting as it does of the sum of the chemical energy of formation of AB and the relative translational energies of A and B before collision, will seldom if ever correspond to a quantised energy level of AB. Therefore, in the absence of a third body which can act as an acceptor of unwanted energy in excess of a suitable, exactly quantised amount, the newly-formed molecule, AB, must dissociate, A and B flying apart in a time comparable to that of collision.

Born and Franck have likewise shown that the third body collision is also necessary when a positive ion combines with a neutral atom or a molecule. Three-body collisions are not essential, though they can play a rôle, when two oppositely charged ions combine, or when a free electron is captured by a neutral atom or molecule; in which cases the ratio of the newly formed particles which lose energy solely by radiation to those whose energy conditions are adjusted by means of colliding third bodies is a function of the pressure. Sir J. Larmor* and Trautz† have pointed out that pure triple collisions in gases must be of such extreme rarity that a purely termolecular gaseous reaction could hardly take place with measurable velocity. It is therefore improbable that the combustion of dry "detonating gas" proceeds as a purely termolecular reaction, because Bone and Weston‡ have shown that a rigidly dried "detonating gas" can be ignited and will then propagate flame. It appears to us, however, that Born and Franck's three-body collision theory may be extended in the following direction:—If neither A nor B is capable of attaching to, and forming loose unstable complexes or compounds with, the third body, C, then the rate of formation of AB will be a function of the frequency with which pure triple, *i.e.*, simultaneous, collisions occur between A, B and C. On the other hand, should either A or B form such a complex with C, then the rate of reaction will necessarily not only be far greater than when pure triple collisions alone are involved, but also proportional to the life of the complex, AC or BC. The mechanism in this latter case is essentially that of a two-body collision, which must, however, be of a type not forbidden by the three-body collision theory, followed by a second two-body collision from which emerge two particles, namely the product of the reaction, AB, and the original third body C. Such a sequence of collisions may, for brevity, be termed an "indirect triple collision."

* 'Manch. Memoir.,' Wilde Lecture (1908).

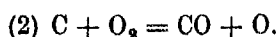
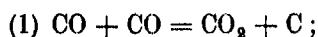
† 'Zeit. f. Elektroch.,' vol. 22, p. 104 (1916).

‡ 'Proc. Roy. Soc.,' A, vol. 110, p. 615 (1926).

Any attempt to explain the facts relating to the cathodic combustion of carbonic oxide by oxygen in terms of the above outlined extension of the three-body collision theory must clearly involve the assumption being made that, apart from auto-oxidation, the carbonic oxide molecule can only be burnt by an atom, as distinct from a molecule, of oxygen. There is considerable evidence to justify such an assumption being made. The spectrographic examination of the discharge in "detonating gas" and in other gases has afforded strong support of the view that atomic oxygen is freely present in both the cathode and interelectrode (when active) zones (V). Further, the view was put forward as far back as 1886 by H. E. Armstrong* that carbonic oxide and oxygen molecules are absolutely inert towards each other.

Dry "detonating gas" and its mixtures with either of its constituents burn exceedingly slowly at non-sputtering cathodes, the value of c/i never exceeding 0.05 (fig. 3 curve tantalum). The only possible third bodies present in this case are carbonic oxide, molecular and atomic oxygen, carbon, electrons (both free and captured by oxygen), carbon dioxide and the surface of the cathode itself. The latter is certainly not essential to combustion, because dry "detonating gas" can burn in the interelectrode zone in the absence of either metal particles or an electrode surface. We conclude, therefore, that the combustion of carbonic oxide-oxygen mixtures at a non-sputtering cathode proceeds as follows:—

In the first place auto-oxidation of CO, with subsequent oxidation of the carbon occurs, thus:

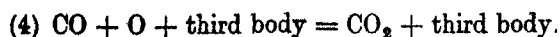


Carbon aggregates, consisting of two or more atoms, can combine with O_2 to form CO_2 directly.

The direct oxidation of CO by oxygen is determined by a prior excitation of the oxygen molecules whereby their internal energy is increased to at least such an extent that, under the conditions of our experiments, dissociation into atoms occurs, thus:—

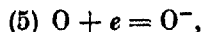


Some combustion of carbonic oxide by oxygen atoms thereupon results from pure triple collisions, thus:—

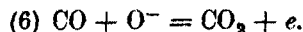


* 'Trans. Chem. Soc.,' vol. 49, p. 112 (1886).

But the chief amount of such direct combustion is due to indirect triple collisions between oxygen atoms, carbonic oxide and electrons, thus :—



and



The mechanism of the cathodic combustion of dry $\text{CO} - \text{O}_2$ mixtures outlined above may well afford a clue to the origin of the faint continuous background previously observed in the spectrograms of electric discharges in "detonating gas" and of the strong continuous spectrum of the flame of carbonic oxide burning in oxygen (V), because (i) the energy associated with the electron in (5) is unquantised, (ii) O_2 , O_2^+ and O^+ can also capture electrons directly, (iii) and O or O^+ and O_2^- , or O_2 and O^- may well react without the necessary intervention of a third body (and we have shown experimentally that ozone is formed in the case under consideration), and finally (iv) carbon formed according to (1) may possibly agglomerate within the discharge, though positive evidence is still lacking on this point. With regard to the consequences following upon (i) to (iii), all these are, or are analogous to, cases of the capture of a free electron by a neutral atom or molecule with the result that, to quote Born and Franck,* "...kontinuierliche Spektren auftreten analog denjenigen, die sich an die Seriengrenzen anschliessen. Natürlich sind auch hier Dreierstösse möglich. Die relative Häufigkeit von Molekülbildung durch Strahlung zu der durch Dreierstoss ist hier eine Funktion des Druckes."

We attribute greater importance to the rôle played by the indirect triple collision, (5) and (6), in the direct combustion of CO , because of the far greater probability of such collisions, and also because Sir J. J. Thomson† has shown that, when neutral oxygen molecules collide with electrons, something of the order of 1.4 to 5.7×10^8 such collisions are sufficient for the formation of one negatively charged oxygen molecule. With oxygen atoms the number of negative ions thus formed must be considerably greater. The number of electrons present at any moment within the cathode zone depends on the current; the amount of atomic oxygen is similarly determined, but it increases also with the concentration of oxygen in the gaseous mixture traversed by the discharge. Therefore, the number of negative oxygen atom ions, while proportional to the number of electrons and

* *Loc. cit.*

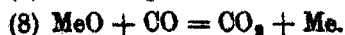
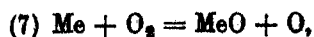
† 'Conduction of Electricity through Gases,' by Sir J. J. and G. P. Thomson, 3rd ed., p. 242 (1928).

hence to the current, will be considerably less than if they had been directly proportional to the oxygen concentration in the mixture alone. Further, from the point of view of their being effective in bringing about the combustion of the carbonic oxide, wastage of both negatively charged and neutral oxygen atoms must be continually occurring as a result of recombination. The carbonic oxide molecule does not form a negative ion and cannot, therefore, combine directly with a neutral oxygen atom in the manner outlined above. Thus this view not only affords a reasonable explanation of the fact that in dry carbonic oxide-oxygen mixtures, containing not more than 80 per cent. of carbonic oxide, and burning at a typical non-sputtering cathode (fig. 3, curve tantalum), the value of c/i decreases slowly with increasing dilution with oxygen; but it is also in accordance with the known facts relating to inter-electrode combustion.

Moisture greatly accelerates the rate of combustion of carbonic oxide at a non-sputtering cathode (fig. 4). In "detonating gas" containing 3 mm. partial pressure of moisture, c/i can under the conditions of our experiments attain a value of 0.29, *i.e.*, about six times greater than that found in the dry mixture. On dilution of such a moist "detonating gas" with carbonic oxide, c/i increases to attain a series of maximum values in a mixture corresponding approximately to $4\text{CO} + \text{O}_2$. On similarly diluting with oxygen, c/i decreases rapidly. Pressure exerts a pronounced negative effect, and, in the equivalent mixture, c/i decreases hyperbolically with increasing pressure. These facts and the observation recorded above to the effect that considerably more hydrogen peroxide is formed during the combustion of moist "detonating gas" at a non-sputtering, than at a freely sputtering cathode, will be discussed in the next communication of this series.

In the combustion of dry "detonating gas" at a freely sputtering cathode, c/i increases with increasing dilution with oxygen from about 0.20 until maximum values are reached in a mixture corresponding in composition to approximately $\text{CO} + 4\text{O}_2$ (figs. 3 and 6). *Ceteris paribus*, c/i increases with increasing pressure, a fact which had previously been observed (III). These facts can be accounted for if it be assumed that in this case combustion proceeds as follows.

In addition to reactions (1) to (6), sputtered metal atoms interact with oxygen molecules to form loose complexes, which thereupon react with carbonic oxide molecules thus:—



On kinetic grounds, since the number of sputtered metal atoms within the cathode zone is directly proportional to the current and independent of the pressure (III), this view affords a reasonable explanation of the fact that the value of c/i increases with either increasing pressure or oxygen dilution.

The results obtained in studying the combustion of moist carbonic oxide-oxygen mixtures at sputtering cathodes afford further confirmation of the fundamentally different nature of the rôles played by steam and metal particles in promoting such combustion (figs. 5 and 7). Between two series of maximum values, one of which was obtained in a mixture containing about 80 per cent. carbonic oxide and the other in one containing between 70 to 80 per cent. oxygen, the c/i curves converge towards a minimum value in a mixture approaching closely in composition to that of "detonating gas." In the region of excess carbonic oxide, the pressure effect is negative; but with excess oxygen, it is positive. Reversal of the pressure effect occurs at or near the minimum point between the two series of maxima, and here c/i is independent of pressure. These facts and their bearing upon the mechanism of the cathodic combustion of carbonic oxide will be fully discussed in the next communication of this series.

The effect of dilution of dry "detonating gas," burning at a freely sputtering cathode, with nitrogen (fig. 1), helium or argon (fig. 2) upon the value of c/i is, in view of the other facts set forth above, such as to leave no room for doubt that these gases were acting as purely physical diluents. The curves for nitrogen lie, indeed, close to, but between those of, helium and argon.

Summary.

In the foregoing experiments it has been shown that :—

(i) An electric discharge can be passed through dry or moist mixtures of carbonic oxide "detonating gas" diluted with nitrogen, helium, argon, carbonic oxide or oxygen in such a manner that carbonic oxide burns at a rate which is determined solely by the current passed by the discharge.

(ii) The rate of cathodic combustion in any such mixture is directly proportional to the current.

(iii) Dilution of dry "detonating gas" with either of its constituents between the limits of 88 per cent. carbonic oxide and 83 per cent. oxygen, has only a slight effect upon the rate of combustion at a non-sputtering cathode, which decreases slowly with increasing percentage concentration of oxygen.

(iv) The rate of combustion of dry "detonating gas" at freely sputtering cathodes (α) is inversely proportional to the amount of dilution with nitrogen,

helium, or argon, and (b) increases on dilution with oxygen up to between 70 and 80 per cent. oxygen and/or with increase in pressure.

(v) The rate of combustion of moist "detonating gas" at a non-sputtering cathode (a) increases on dilution with carbonic oxide up to 80 per cent. carbonic oxide, but (b) decreases with increasing pressure.

(vi) At freely sputtering cathodes, moist "detonating gas" burns at a rate which is independent of pressure; but dilution with either carbonic oxide or oxygen increases this rate; in the former case the pressure effect is negative, in the latter positive.

(vii) Hydrogen peroxide is formed when moist "detonating gas" is burnt cathodically; the amount thereof being greater at a non-sputtering than at a freely sputtering cathode.

(viii) Free hydrogen is formed during the cathodic combustion of moist $\text{CO} - \text{O}_2$ mixtures.

(ix) Auto-oxidation of carbonic oxide occurs within the cathode zone.

From these and previously established facts and from considerations arising out of the three-body collision theory it is concluded that:—

- (i) Carbonic oxide is auto-oxidised, the carbon thus formed being burnt directly by oxygen.
- (ii) The fundamental mechanism of the direct combustion of carbonic oxide by oxygen consists in the union of carbonic oxide molecules with oxygen atoms in either pure or indirect triple collisions.
- (iii) Metal atoms combine with oxygen molecules to form loose complexes which readily oxidise carbonic oxide.

One of us (W.L.P.) wishes to thank the Derbyshire Education Committee, the Trustees of the Risley Education Foundation, the Board of Education, and the Department of Scientific and Industrial Research for grants which have enabled him to devote his full time to this research. Our thanks are also due to the Government Grants Committee of the Royal Society for a grant with which the cost of some of the apparatus employed in this investigation was defrayed.

Gaseous Combustion in Electric Discharges. Part VII.—The Effect of Dilution with Hydrogen on the Cathodic Combustion of Carbonic Oxide—Oxygen Mixtures.*

By G. I. FINCH and W. L. PATRICK, Imperial College of Science.

(Communicated by W. A. Bone, F.R.S.—Received July 14, 1930.)

Introduction.

The fact that hydrogen is formed during the cathodic combustion of moist "detonating gas" † (VI) suggests that carbonic oxide can be burnt by steam in the discharge. To test this view, systematic investigations along the following three lines were undertaken:—A study of (i) the effect of hydrogen on the cathodic combustion of carbonic oxide, (ii) the cathodic equilibrium between steam and carbonic oxide, and (iii) the cathodic combustion of mixtures of hydrogen and oxygen in various proportions. In what follows is given an account of the investigation of the effect of dilution with hydrogen on the cathodic combustion of "detonating gas."

The experimental results have shown, *inter alia*, that hydrogen is, in the absence of sputtered metal atoms, a more powerful promoter of the cathodic combustion of carbonic oxide than steam, and that more carbon dioxide than steam is formed when a mixture of carbonic oxide, hydrogen and oxygen in equal proportions is burnt cathodically. These and the further facts set forth below, considered in conjunction with those previously established in the course of the preceding investigations of this series, have enabled us to put forward in what follows a view of the mechanism of the cathodic combustion of carbonic oxide and of the rôle played therein by hydrogen, steam and metal particles, which is not only in accordance with the said facts, but also appears to us to afford a satisfactory basis for a reasonable explanation of the known facts relating to the combustion of carbonic oxide in flames in general.

* 'Proc. Roy. Soc.,' A, vol. 129, p. 656 (1930), Part VI, wherein full references are given for the preceding parts of this series. For brevity, these are referred to in the above communication by their respective Roman numerals within brackets.

† A mixture of carbonic oxide and oxygen in their combining proportions will be referred hereinafter as "detonating gas."

Experimental.

The experiments were carried out in the circulation apparatus (III, see figure on p. 306), to which a mercury-filled gas sampling eudiometer had been added by means of a T-piece blown into the tube connecting the phosphoric oxide drying tube, Q, with the gas entrant end of the combustion vessel, R.

The gaseous mixtures employed were prepared by mixing carbonic oxide, oxygen and electrolytic gas in the desired proportions and were stored in steel gasholders over dry mercury. The proportions were checked immediately before use in a Bone-Newitt gas analysis apparatus. The mixtures were dried in all the experiments to be described below by passage through a 60-cm. long tube, containing purified phosphoric oxide, prior to entering the combustion vessel.

Gold or tantalum electrodes which had been used in the experiments described in Part VI were employed. The gap width, current and pressure ranges chosen were such as to exclude interelectrode combustion, without at the same time giving rise to distortion of the cathode glow.

The Experimental Results.

Series I.—The object of these experiments was to determine the relative rates of cathodic combustion of carbonic oxide and hydrogen with oxygen in a mixture containing equal proportions of the three gases. The initial total gaseous pressure at the beginning of each experiment was 120 mm. Samples of the partly burnt mixtures were withdrawn for analysis at various known pressures. After each sampling, the circulation system was evacuated and refilled with the $\text{CO} + \text{O}_2 + \text{H}_2$ mixture to 120 mm. and a fresh run commenced. Combustion was carried out at tantalum (non-sputtering) and gold (freely sputtering) cathodes. The gap width was 1.2 mm. and the current range between 2.55 and 3.65 milliamperes. For purposes of comparison, the values of c/i (the ratio of the rate of combustion of electrolytic gas in cubic centimetres at N.T.P. per minute to current in milliamperes) obtained with tantalum and gold cathodes were then determined in further experiments. The results are incorporated in Tables I and II.

Table I.—Showing the Change in Composition of the Original ($\text{CO} + \text{O}_2 + \text{H}_2$) Mixture during Combustion.

Total gaseous pressure in mm	Tantalum cathode.			Gold cathode.		
	O_2	CO	H_2	O_2	CO	H_2
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
120	33.3	33.3	33.3	33.3	33.3	33.3
80	33.5	32.2	34.3	33.0	28.2	38.8
60	33.0	31.3	35.7	33.3	24.2	42.5
30	31.0	27.1	42.0	32.4	9.4	58.2

Table II.— c/i Values for the Cathodic Combustion of "Detonating Gas" (from Part III), of Electrolytic Gas and of ($\text{CO} + \text{O}_2 + \text{H}_2$); all mixtures being dry.

Total gaseous pressure in mm.	$2\text{CO} + \text{O}_2$		$2\text{H}_2 + \text{O}_2$		$\text{CO} + \text{O}_2 + \text{H}_2$	
	Ta ⁻ .	Au ⁻ .	Ta ⁻ .	Au ⁻ .	Ta ⁻ .	Au ⁻ .
90	0.045	0.25	0.30	0.25	0.38	0.34
60	0.045	0.24	0.29	0.24	0.38	0.34
30	0.045	0.24	0.28	0.23	0.38	0.34
25	0.045	0.23	0.28	0.23	0.38	0.28

Series II.—The results of the analyses incorporated in Table I show that, with decreasing pressure, the oxygen content of the gaseous mixture falls below 33.3 per cent., a value which should be independent of pressure, provided only carbon dioxide and steam had been formed as the final products of combustion. It is clear, therefore, that, in addition to the main products of combustion (CO_2 and H_2O), more highly oxygenated compounds had been formed and removed on circulation. A qualitative examination of the products of the cathodic combustion of a ($\text{CO} + \text{O}_2 + \text{H}_2$) mixture revealed the presence of considerable amounts of hydrogen peroxide and of some ozone in the combustion products, in addition to carbon dioxide and steam. Accordingly, a series of experiments were carried out in which steps were taken to determine the amounts of hydrogen peroxide formed during the cathodic combustion of several gaseous mixtures the compositions of which are given in Table III.

The quantitative estimation of hydrogen peroxide was carried out colorimetrically with acid titanous sulphate solution in the manner previously described (VI). Ozone in the combustion products was detected qualitatively by means

of a test paper, moistened with an alcoholic solution of tetramethyl-dipara-diamino-diphenyl methane (tetramethyl base) and inserted in the circulation system immediately after the combustion vessel. The initial total gaseous pressure was in all cases 120 mm., and the mixtures were burnt cathodically until the pressure had fallen to 30 mm. The further necessary experimental data and the results are incorporated in Table III. Ozone was detected in every case. It had, indeed, been frequently observed in the course of these investigations that the mercury in the circulating pump, and more particularly that in the valves, was much more quickly fouled when dry carbonic oxide-oxygen mixtures were burnt than when such mixtures contained moisture or hydrogen.

Table III.—Showing the Amount of Hydrogen Peroxide formed during Cathodic Combustion.

Gaseous mixture.	Percentage of original oxygen recovered as hydrogen peroxide.	
	Tantalum cathode.	Gold cathode.
$2\text{H}_2 + \text{O}_2$	0.18	0.06
$\text{CO} + \text{O}_2 + \text{H}_2$	0.80	0.19
$2\text{CO} + \text{O}_2 + 0.33\text{O}_2 + 3 \text{ mm. (H}_2\text{O)}$	0.06	0.02

Series III.—In the experiments of this series, which were carried out in a manner similar to those of Series I, the cathodic combustion of a ($2\text{CO} + \text{O}_2 + 2\text{H}_2$) mixture at tantalum and gold electrodes was studied. The gap width was 1 mm. and the current range between 1.82 and 2.55 milliamperes. The initial total gaseous pressure was 100 mm. The results are given in Table IV.

Table IV.—Showing the Change in Composition of the Original $2\text{CO} + \text{O}_2 + 2\text{H}_2$ Mixture and the Variation of c/i during Combustion.

Total gaseous pressure in mm.	Tantalum cathode.				Gold cathode.			
	O_2	CO	H_2	c/i	O_2	CO	H_2	c/i
	per cent.	per cent.	per cent.		per cent.	per cent.	per cent.	
100	20	40	40	0.50	20	40	40	0.255
90	—	—	—	0.52	—	—	—	0.255
80	—	—	—	0.54	—	—	—	0.255
70	—	—	—	0.58	—	—	—	0.255
60	10.5	39.7	49.8	0.67	10.8	35.5	53.6	0.255
50	9.7	40.9	49.4		11.2	35.0	53.7	
50	—	—	—	0.67	—	—	—	0.255
Between 40 and 41	0.2	35.3	64.5	practically zero	0.6	28.4	70.9	practically zero
	0.3	35.1	64.6		0.5	29.8	69.9	

Series IV.—We now proceeded to study the effect of smaller additions of hydrogen, than had hitherto been employed, on the cathodic combustion of "detonating gas." The results of these experiments are set forth in Tables V and VI. The initial total gaseous pressure was 100 mm. in all experiments. Current range and gap width were as in Series III. The curves shown in fig. 1 bring out more clearly the remarkable difference between the effect of the dilution of dry "detonating gas" with hydrogen or steam upon cathodic combustion occurring at tantalum or gold electrodes. These curves have been constructed from the experimental results set forth in this and in previous communications (IV and VI).

Table V.—Showing the Effect of Dilution with Hydrogen on the Value of c/i in the Cathodic Combustion of Dry "Detonating Gas" at Tantalum.

Total gaseous pressure in mm.	Initial hydrogen contents of the mixture at 100 mm. in per cent.					
	0.	1.	3.	7.	15.	40.
100	} 0.045 {	0.09	0.16	0.26	} 0.40 {	0.50
90		0.09	0.15	0.24		0.52
80		0.09	0.14	0.22		0.54
70		0.085	0.13	0.19		0.58
60		0.080	0.11	0.18		0.67
50		0.08	0.09	0.16		0.67
40		0.08	0.08	0.14		—
30		0.08	0.07	0.12		—

Table VI.—Showing the Effect of Dilution with Hydrogen on the Value of c/i in the Cathodic Combustion of Dry "Detonating Gas" at Gold.

Total gaseous pressure in mm.	Initial hydrogen contents of the mixture, at the initial pressure of 100 mm., in per cent.					
	0.	1.	3.	7.	15.	40.
90	0.25	0.25	0.25	0.27	0.28	0.255
60	0.24	0.245	0.25	0.27	0.28	0.255
30	0.24	0.24	0.25	0.27	0.28	—

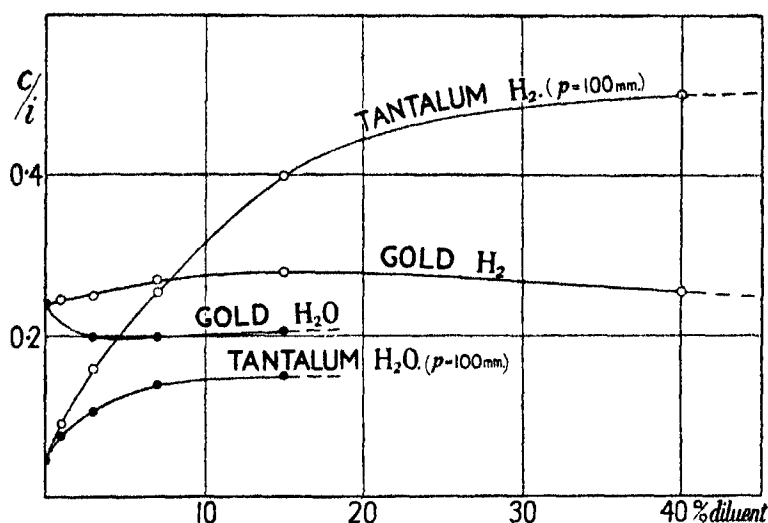


FIG. 1.—The Effect of Dilution with Equivalent Amounts of H_2 or H_2O on the Rate of Cathodic Combustion of a $(2CO + O_2)$ Mixture.

Discussion of the Results.

The experimental results set forth in Tables I and IV directly establish the fact that, except in the case of extreme dilution with one or other of the combustible constituents, $CO - O_2 - H_2$ mixtures containing no more than sufficient oxygen for complete combustion burn cathodically at either tantalum or gold in such a manner that the relative proportion of carbon dioxide to steam in the combustion products is greater than the corresponding proportion of carbonic oxide to hydrogen in the original unburnt mixture. Thus, the final result of whatever reactions may occur within the cathode zone is such that, under the conditions stated, carbonic oxide appears to burn therein more readily than does hydrogen. But the fact that, as is shown in Table II, the rate of combustion of dry "detonating gas" at a non-sputtering cathode is less than one-sixth of that of dry electrolytic gas burning under similar conditions proves that hydrogen is, on the contrary, burnt cathodically by oxygen much more readily than is carbonic oxide. Therefore, the preferential cathodic combustion of carbonic oxide in $CO - O_2 - H_2$ mixtures can only be due to the prior formation within the cathode zone of some product (or products) of the combustion of hydrogen which is capable of oxidising carbonic oxide more readily than does oxygen, and which in so doing is thereby itself reduced, to some extent at least, to free hydrogen.

The results of the quantitative gas analyses incorporated in Table I and in

the second horizontal column of Table III prove that the sole products of the cathodic combustion of a $(\text{CO} + \text{O}_2 + \text{H}_2)$ mixture are, in addition to carbon dioxide and traces of ozone, steam and hydrogen peroxide. Therefore, carbonic oxide is oxidised more readily by freshly formed steam or hydrogen peroxide, or by both, than by oxygen. It should not be overlooked, however, that OH may be present within the discharge (V). It may well be that OH is capable of readily oxidising CO.

The results incorporated in Table III show that, when electrolytic gas or a $(\text{CO} + \text{O}_2 + \text{H}_2)$ mixture or moist "detonating gas" is burnt cathodically, at least three times as much hydrogen peroxide can be recovered from the combustion products leaving a non-sputtering cathode zone as when the cathode is a freely sputtering metal. This fact can only mean that either metal atoms promote the combustion of hydrogen to steam in preference to H_2O_2 , or that such atoms decompose some of the H_2O_2 formed within the cathode zone. In view of the facts that the rates of combustion of electrolytic gas at gold and tantalum show only a slight difference, it would seem that sputtered gold decomposes H_2O_2 , but does not actually inhibit its formation to any great extent. It is well known that colloidal metal solutions or suspensions of finely divided metals are able to effect the explosive decomposition of concentrated hydrogen peroxide solutions.

The results incorporated in Table IV establish the facts that the combustion of a $2\text{CO} + \text{O}_2 + 2\text{H}_2$ mixture proceeds far more rapidly at a tantalum than at a gold cathode. This proves that, in the mixture under consideration, both freshly formed steam and hydrogen peroxide oxidise carbonic oxide within the cathode zone much more readily than does oxygen.

The results of the analyses given in Tables I and IV establish the fact that the preferential combustion of carbonic oxide in $\text{CO} - \text{O}_2 - \text{H}_2$ mixtures, containing no more oxygen than suffices for complete combustion, is more pronounced at a freely sputtering (gold) cathode than at a non-sputtering (tantalum) cathode. The conclusion may, therefore, be drawn that steam and hydrogen peroxide oxidise carbonic oxide in such a manner that, in addition to CO_2 , hydrogen and steam are formed respectively.

The values of c/i for the cathodic combustion of $\text{CO} - \text{O}_2 - \text{H}_2$ mixtures of the range of compositions given in Table IV are 0.255 and between 0.50 and 0.67 at gold and tantalum cathodes respectively. We may, therefore, conclude that a large proportion of the hydrogen burns to H_2O_2 , because otherwise the extent to which CO would have been burnt preferentially must have been much greater.

The extent to which preferential combustion of CO occurred at a tantalum cathode (Tables I and IV) proves that steam resulting from the reduction of H_2O_2 by CO is inactive—i.e., is unable to oxidise CO without further activation by the electric discharge or by some other suitable means. It was shown above that H_2O freshly formed by the combustion of H_2 is, on the other hand, active.

A comparison drawn between the effects of equivalent amounts of H_2 and H_2O on the rate of combustion of a $(2\text{CO} + \text{O}_2)$ mixture at a tantalum cathode (see fig. 1) enables the conclusion to be drawn that hydrogen, freshly formed by the reduction of steam by CO, is in a specially active condition and will burn readily with little, or even without further, excitation by the electric discharge, but, in so doing, burns to a large extent to H_2O_2 . This conclusion is supported by the fact, amongst others, that certain $\text{CO} - \text{O}_2 - \text{H}_2$ mixtures (see Table IV) burn cathodically at a tantalum electrode more than twice as rapidly as any of the dry or moist $\text{CO} - \text{O}_2$ or $\text{H}_2 - \text{O}_2$ mixtures burn at a gold cathode, and the combustion of which we have so far studied. This conclusion also explains the fact that an electric discharge can be passed through, and slow combustion determined in, $\text{CO} - \text{O}_2 - \text{H}_2$ mixtures, under such conditions of pressure that flame can be propagated therein, without explosion occurring. Were such active H_2 to burn mainly to steam, this would, as has been shown above, be active and thus would lead to the setting up of a self-propagating chain reaction.

The results of the analyses shown in Tables I and IV establish the fact that the preferential combustion of CO in $\text{CO} - \text{O}_2 - \text{H}_2$ mixtures becomes more pronounced with decreasing pressure. This fact is brought out clearly in fig. 2. In the light of the above facts and conclusions, this can only mean that the ratio $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ increases with increasing pressure—i.e., an increase in pressure favours the cathodic combustion of H_2 to H_2O_2 , while a decrease in pressure favours the formation of steam.

The results incorporated in fig. 2 further establish the fact that the preferential combustion of CO in $\text{CO} - \text{O}_2 - \text{H}_2$ mixtures at either tantalum or gold cathodes—and, therefore, the combustion of hydrogen to steam—is favoured by an increase in the concentration of hydrogen and/or a decrease in the concentration of O_2 . Similarly, it may be concluded that the formation of H_2O_2 increases with increasing concentration of oxygen.

In Table V are given results which show the effect of increasing dilution with hydrogen on the value of c/i for the combustion of dry “detonating gas” at a tantalum cathode. Quantitative analyses of the gaseous mixtures at different stages of combustion, other than at the beginning of each experiment,

were not carried out. In view of the results of the analyses incorporated in Tables I and IV, however, it may be safely concluded that the percentage

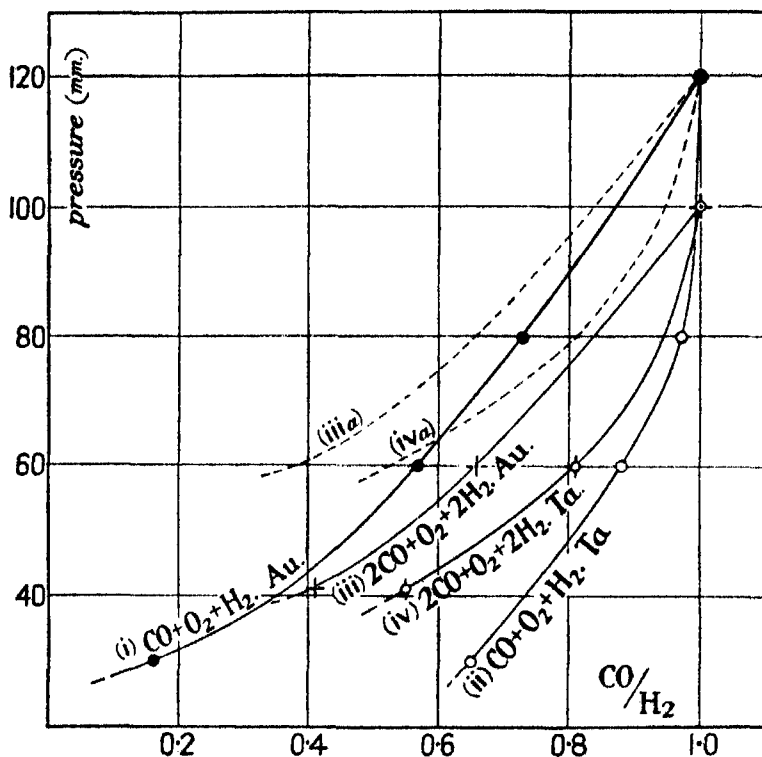
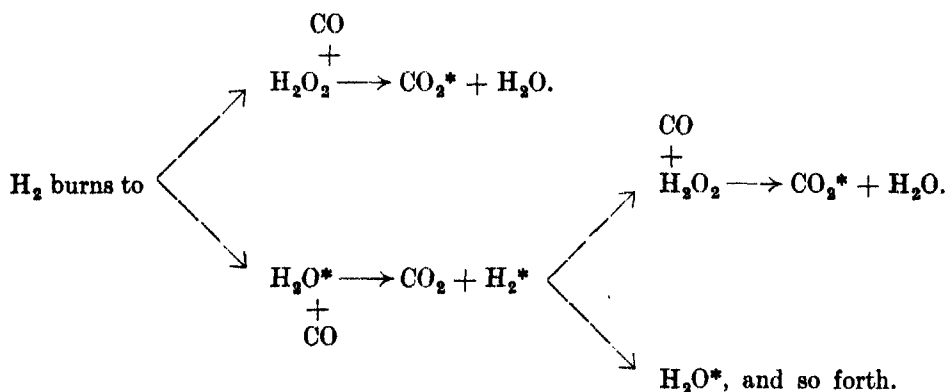


FIG. 2.—The effect of Pressure on the Preferential Cathodic Combustion of CO — O₂ — H₂ Mixtures. The broken curves (iii_a and iv_a) have been obtained by transposing curves iii and iv from an initial pressure of 100 to one of 120 mm., thus enabling the slopes of all curves to be compared more readily.

concentration of H₂ in each experiment never fell below its initial concentration, but, on the contrary, almost certainly increased as combustion proceeded. Therefore, the facts that the rate of combustion of the "detonating gas" (i) decreases with decreasing pressure when up to 7 per cent. of hydrogen is present, (ii) is independent of pressure with 15 per cent. H₂ and (iii) increases with decreasing pressure when diluted with 40 per cent. H₂, can be due only to the effect of pressure and not to changes in the concentration of H₂ occurring during combustion in the individual experiments. These striking facts are readily explained, because it has been shown above that, when hydrogen is burnt cathodically, increasing pressure and/or oxygen concentration favour the formation of H₂O₂, and decreasing pressure and/or decreasing oxygen

concentration and/or increasing hydrogen concentration favour the formation of steam.

Finally, the values of c/i for the combustion of dry CO — O₂ mixtures diluted to various extents with H₂ (Tables V and VI), together with the facts and conclusions outlined above, strongly suggest that the rôle played by hydrogen in promoting the combustion of CO under the conditions of our experiments may be outlined as follows:—



The conclusion as to whether the CO₂ is highly excited or not is drawn directly from well-known thermo-chemical data and from the facts and conclusions outlined above.

Of the two modes of oxidation of CO by steam and H₂O₂ respectively, it is clear that the former, whereby active steam oxidises CO directly, should be much the more active process of the two. This view is generally supported by the facts relating to the cathodic combustion of carbonic oxide as hitherto established in the course of these investigations, and is in complete agreement with the conclusion drawn above that much the same relative proportions of steam and H₂O₂ are formed at tantalum and gold electrodes under otherwise similar experimental conditions, but that by far the greater part of such H₂O₂ is decomposed into inactive steam and atomic oxygen at the sputtering cathode by metal atoms.

Thus, according to this view, under the conditions of our experiments, H₂ burns to a large extent to H₂O₂, and combustion is non-self-propellant because the chains of reactions outlined above soon come to an end. But where conditions are such as to favour the formation of active steam, either by the

* Signifies a highly active (excited) molecule.

oxidation of H_2 or by dissociation of H_2O_2 and subsequent activation of the water formed thereby, then the unbroken chain reaction combustion of CO by steam occurs and leads to explosion.

Far more H_2O_2 survives in, and is recoverable from, the products of the cathodic combustion of a $(CO + O_2 + H_2)$ mixture than from those of electrolytic gas (Table III). This fact affords strong support for the view of the mechanism of the combustion outlined above, since, according to that view, hydrogen, in the absence of CO, burns to a mixture of steam and H_2O_2 , whereas, when CO is present, H_2O_2 is re-formed in the course of the ensuing chain reactions.

It is our intention to develop this view of the combustion of carbonic oxide

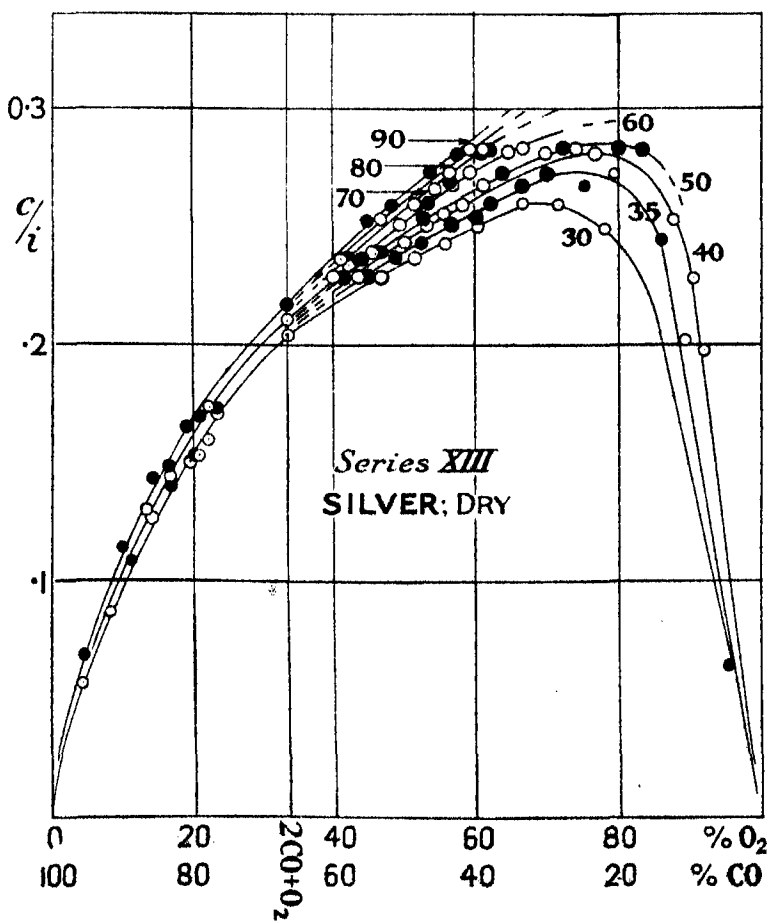


FIG. 3.—Cathodic Combustion of Dry CO — O_2 Mixtures. The numbers assigned to the curves denote total pressures in millimetres.

in a further communication to the Society, and to show in detail how it affords a reasonable explanation of the known facts of the combustion of carbonic oxide in flames generally, and of the rôles played by steam, hydrogen and metal particles in promoting such combustion.

It is now possible, in the light of the experimental results set forth above, to put forward an explanation of the results obtained during the investigation of the combustion of moist CO — O₂ mixtures at a freely sputtering cathode (VI). The results then obtained with a silver cathode are shown in figs. 3 and 4. They closely resemble in all essential features those obtained with gold (VI). In view of the facts outlined above, the following explanation of the effect of

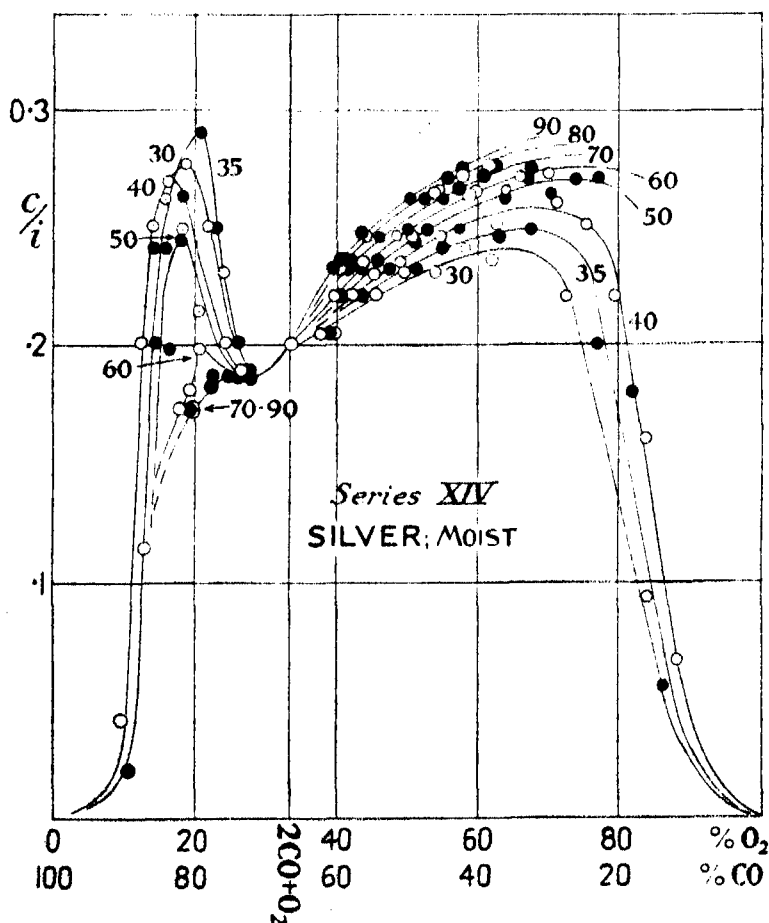


FIG. 4.—Cathodic Combustion of Moist CO — O₂ Mixtures. The numbers assigned to the curves denote total pressures in millimetres.

steam upon the cathodic combustion of "detonating gas" may be put forward.

Some of the inactive steam present in the mixture is activated by the discharge and reacts with CO. The resulting active H_2 burns to H_2O_2 and active steam. When CO is present in excess in the mixture, which is then deficient in O_2 , the conditions are such as to favour the combustion of hydrogen to steam. The value of c/i accordingly increases with decreasing pressure. In the presence of excess O_2 , hydrogen burns preferentially to H_2O_2 , but this is largely decomposed by metal particles and under these circumstances the cathodic combustion of CO is brought about mainly by the intervention of sputtered metal atoms, in the manner outlined in (VI), and to a considerably lesser extent by active steam.

Summary.

In the foregoing experiments it has been shown that:—

(i) $CO - O_2 - H_2$ mixtures burn cathodically in such a manner that (a) the rate of combustion is proportional to the current, (b) the value of the ratio CO_2/H_2O in the reaction products is greater than that of the CO and H_2 contents of the original mixture, (c) such preferential combustion of CO is more pronounced at a freely sputtering than at a non-sputtering cathode.

(ii) Electrolytic gas burns about six times more rapidly at a non-sputtering cathode than does dry CO—"detonating gas."

(iii) The products of combustion, at a non-sputtering cathode, of electrolytic gas, of moist "detonating gas" diluted with oxygen and of a $(CO + O_2 + H_2)$ mixture contain more H_2O_2 than when a freely sputtering cathode is employed.

(iv) H_2 is a more powerful promoter of the cathodic combustion of CO than is steam.

(v) The effect of pressure on the rate of combustion with small additions of H_2 is negative, but positive with larger additions when combustion proceeds at a non-sputtering cathode.

(vi) Electrolytic gas, "detonating gas" and $CO - O_2 - H_2$ mixtures, containing not more than sufficient oxygen for the complete combustion of one-half of the combustible constituents, all burn at a gold cathode at nearly the same rate; such rate being practically independent of pressure.

(vii) The preferential combustion of CO in $CO - O_2 - H_2$ mixtures becomes more pronounced with decreasing pressure.

From these facts the conclusions are drawn that:—

(i) The cathodic combustion of $CO - O_2 - H_2$ mixtures proceeds in such a manner that hydrogen burns, first, to active steam and H_2O_2 , both of

which then oxidise CO more readily than does oxygen, whereby the former is reduced to an active form of hydrogen and the latter to inactive steam. Some direct oxidation in the manner outlined in (VI) may also occur, depending upon the conditions of pressure and hydrogen concentration.

- (ii) Sputtered metal atoms decompose H_2O_2 to inactive steam.
- (iii) Active H_2 burns readily to active steam and H_2O_2 .
- (iv) CO burns with H_2O_2 to highly activated CO_2 and inactive steam.
- (v) Active steam burns with CO to inactive CO_2 and active hydrogen.
- (vi) Increasing pressure and/or oxygen concentration favours the combustion of H_2 to H_2O_2 .
- (vii) Decreasing pressure and/or decreasing oxygen concentration and/or increasing hydrogen concentration favours the combustion of H_2 to active steam.

It is our intention to show in a future communication to the Society that there is no fundamental difference between cathodic combustion and combustion in flames in general, and that the reactions taking place in both cases are homogeneous. We intend, further, to develop the view outlined above and in (VI), and to show in detail how it affords a reasonable explanation (i) of the facts concerning the combustion in flames of carbonic oxide and the rôle played therein by hydrogen, steam, metal particles and pressure, and (ii) of the fact that rigid drying does not reduce to any pronounced extent the ignitability of, and rate of propagation of flame in, combustible mixtures containing hydrocarbons, cyanogen, hydrogen sulphide or carbon disulphide.

One of us (W.L.P.) wishes to thank the Derbyshire Education Committee, the Trustees of the Risley Education Foundation, the Board of Education, and the Department of Scientific and Industrial Research for grants which have enabled him to devote his full time to this research. Our thanks are also due to the Government Grants Committee of the Royal Society for a grant with which the cost of some of the apparatus employed in this investigation was defrayed.

The Interaction of Inert Gases.

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Introduction.

The following paper studies from a quantum mechanical point of view a special kind of chemical reaction, namely, the inertness of the inert gases. In the development of the quantum theory of homopolar binding this chapter has hitherto been omitted for the following reason: not only is the charge distribution of an inert gas atom spherically symmetrical, but the whole ψ -function, which depends in the case of n electrons on $3n$ space co-ordinates and n spin co-ordinates, is invariant under a simultaneous orthogonal transformation of all co-ordinates. This means that there is no space degeneracy. If now this atom is brought near to another similar one, the disappearance of direction symmetry is not followed by a disappearance of degeneracy—the stationary state does not split up into several states as in most cases of chemical binding, but remains single and seems to correspond, under ordinary conditions, to repulsion.

On the other hand, Heitler and London in their well-known treatment of the H_2 -problem, found that it was just the removal of a degeneracy, which they called “exchange degeneracy,” which gave rise to large resonance forces and thus led to binding in one of the resultant states and repulsion in the other. This induced subsequent workers to suppose that the antiparallel coupling of two electron spins in different atoms always entails a binding force. This was supported from the theoretical side by the fact that the interaction energy could actually be worked out as a sum of terms each belonging to such a coupling. Such a theory could not fail to fit the experiments as it established the rules of Lewis’ theory of electron pairs—a theory already proved to have wide validity.

The quantitative values of these binding forces—the so-called exchange integrals—were often discussed, but little could be done to work them out because the states of the single atoms were not well enough known, and the actual integrations involved offered almost unsurmountable difficulties.

Meanwhile Heisenberg in his theory of Weiss’ forces came to the conclusion that in the case of ferro-magnetic substances the exchange integrals must

have just the opposite sign from those occurring in the first simple theories of homopolar binding and he brought forward arguments to show that this may happen in higher atoms.

On the other hand it became more and more evident that the interaction of the L-vectors of different atoms must play a very similar rôle to that of the S-vectors, as it underlies resonance forces of exactly the same kind. Binding valencies may, therefore, be just as well connected with the existence of electronic angular momentum; and quite possibly one of the oxygen-valencies may best be interpreted in this way, as Lennard-Jones* has pointed out.

In these discussions, however, the existence of closed shells was always neglected because they offer no degeneracy, and therefore no resonance and valency-binding. But this evidently goes too far. There exist exchange-integrals, although there is no degeneracy as we will show subsequently in detail. This was taken into account in a previous paper by the author on Li_2 , and it was found that in this case the K-shells could rightly be neglected in a rough approximation. But obviously this cannot always be so. If we pass over to the halogens we see immediately that however the single valency may be interpreted, all seven electrons of the outermost shell must play an important part in the resulting energy. In fact, it seems reasonable to regard the binding of the halogens as one step removed from the repulsion of the inert gases. This problem, suggested to me by Prof. Lennard-Jones, will be considered in detail in a subsequent paper. Here we will confine ourselves to the treatment of the chemical interaction of completed shells, as a necessary preliminary step.

§ 1. *Orthogonal Invariants of Spherical Harmonics.*

In order not to interrupt the discussion afterwards, we will prove here a theorem on spherical harmonics. It is intimately related to the well-known addition theorem, but the proofs, which are generally given, fail to elucidate the very simple meaning of it.

The differential equation for $f(\vartheta, \phi)$:

$$\frac{1}{\sin \vartheta} \left[\frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial f}{\partial \vartheta} \right) + \frac{\partial}{\partial \phi} \left(\frac{1}{\sin \vartheta} \frac{\partial f}{\partial \phi} \right) \right] + \lambda f(\vartheta, \phi) = 0,$$

has the eigenvalues $\lambda = l(l+1)$ and for each l a set of $2l+1$ eigenfunctions $Y_l^m(\vartheta, \phi)$ ($m = -l, \dots, +l$)—that is, Laplacian spherical harmonics, which

* 'Trans. Faraday Soc.,' vol. 25, p. 668 (1929).

we may assume orthogonal and normalised* (for convenience, we normalise to 4π)

$$(Y_l^m, Y_l^{m'}) = 4\pi \delta_{ll'} \delta_{mm'}.$$

A single set with fixed l :

$$Y_l^m(\vartheta, \phi) \quad (m = -l, \dots, +l),$$

is obviously invariant under any rotation O (as the differential equation has directional symmetry):

$$OY_l^m = \sum_{m'} O_{mm'} Y_l^{m'},$$

where $O_{mm'}$ is an orthogonal matrix, because the set Y_l^m does not lose its orthogonality in a simultaneous rotation round an arbitrary axis.

We have therefore:

$$\sum_m O_{mm'} \bar{O}_{mm''} = \delta_{m'm''}. \quad (1)$$

Let us now consider the function of two points on the sphere:

$$K_l(1, 2) = \sum_m Y_l^m(\vartheta_1, \phi_1) \cdot \bar{Y}_l^m(\vartheta_2, \phi_2). \quad (2)$$

K_l is an orthogonal invariant. To prove this apply the operator O (N.B.—simultaneously on point 1 and point 2).

$$OK_l = \sum_m OY_l^m(1) \cdot \bar{OY}_l^m(2) = \sum_m \sum_{m', m''} O_{mm'} \bar{O}_{mm''} Y_l^{m'}(1) \bar{Y}_l^{m''}(2).$$

But summation over m , gives, according to (1)

$$OK_l = \sum_{m'} Y_l^{m'}(1) Y_l^{m'}(2) = K_l.$$

K_l therefore depends only on the relative position of 1 and 2, that is, on their distance apart on the unit sphere (12):

$$K(1, 2) = f(12).$$

To work out $f(12)$, we place 1 on the pole of the sphere: $\vartheta_1 = 0$, and $\vartheta_2 = (12)$. Now, all the $Y_l^m(\vartheta, \phi)$ vanish for $\vartheta = 0$, except $Y_l^0(0, \phi) = \sqrt{2l+1}$. We get, therefore

$$K_l(1, 2) = \sqrt{2l+1} Y_l^0(12).$$

$Y_l^0(12)$, furthermore, is identical with the Legendre polynomial of order l ,

* (f, g) means throughout the paper the scalar product—

$$(f, g) = \int \bar{f}(x) g(x) dx \quad \text{and} \quad \delta_{ik} = \begin{cases} +1 & \text{for } i = k, \\ 0 & \text{for } i \neq k. \end{cases}$$

apart from a numerical factor $\sqrt{2l+1}$ which arises from the altered area over which we normalise.

Therefore

$$K_l(1, 2) = (2l+1) P_l[\cos(12)]. \quad (3)$$

It is on this simple property of spherical harmonics that the subsequent discussion of spherically symmetrical atoms in a ^1S -state depends.

Incidentally we may remark that the set

$$Y_l^m(\vartheta, \phi) \quad (m = -l, \dots, +l)$$

has two more orthogonal invariants. Firstly,

$$\sum_m |Y_l^m|^2 = \text{const.} \quad (4)$$

which may also be considered as a special case of (3) when the distance (12) vanishes, and which means physically the spherical symmetry of charge distribution. Secondly, the determinant

$$\psi(1, \dots, 2l+1) = \begin{vmatrix} Y_l^{-l}(1) & \dots & Y_l^l(1) \\ \vdots & & \vdots \\ Y_l^{-l}(2l+1) & \dots & Y_l^l(2l+1) \end{vmatrix} \quad (5)$$

which represents the eigenfunction of a completed shell. There seem to exist no more algebraic independent invariants.

For an example, we take $l=1$. We have then :

$$\begin{aligned} Y_1^1 &= \sin \vartheta e^{i\phi} \cdot \sqrt{\frac{3}{2}}, \\ Y_1^0 &= \cos \vartheta \cdot \sqrt{3}, \\ Y_1^{-1} &= \sin \vartheta e^{-i\phi} \cdot \sqrt{\frac{3}{2}}. \end{aligned} \quad (6)$$

In this case

$$K_1(12) = 3 \cos(12), \quad (7)$$

and

$$\psi(1, 2, 3) = 2i \sin(12) \cdot \sin(13) \cdot \sin(213) \quad (8)$$

which is the so-called Sine of the solid angle subtended by 123 at the origin, and is proportional to the volume of the tetrahedron O123.* We conclude at once from this interpretation that the determinant always vanishes when 1, 2 and 3 and the origin lie in the same plane.

* von Staudt, 'Crelles J.,' vol. 24, p. 252 (1842).

§ 2. *Representation of the Atom.*

A suitable approximation of the atomic state forms the basis from which the chemical problem may be attacked. The difficulty of finding one has so far been the chief obstacle in the further development of chemical theory. But due to the work of Slater, Zener, Hartree and Fock, the atomic problem has now been solved in principle, and also some numerical work of wider applicability has been prepared.

The line on which approximation is looked for may be described in the following way.

Our atom has n electrons with the co-ordinates $x_1, \dots, x_n$ where x_1 represents x_1, y_1, z_1, s_1 . Its state

$$\psi(x_1, \dots, x_n)$$

must be written as a *single* determinant of n functions

$$\psi = \begin{vmatrix} f_1(x_1) & . & . & . & f_1(x_n) \\ . & & & & . \\ . & & & & . \\ . & & & & . \\ f_n(x_1) & . & . & . & f_n(x_n) \end{vmatrix} \quad (9)$$

Now the Schrödinger equation

$$H\psi = E\psi \quad (10)$$

can only be solved approximately under this assumption. For the exact solution, the expression

$$\frac{(\psi, H\psi)}{(\psi, \psi)} \quad (11)$$

would be a minimum. This is the variation problem corresponding to the Eulerian equation (10). We can now impose on this variation problem the restriction (9), and Fock has shown how this leads to a set of simultaneous *differential equations* which are similar to those used by Hartree but contain also the exchange terms.

Zener, on the other hand, has solved the problem (11) directly subject to the restriction (9) for all the elements of the first row of the periodic system, assuming special types of functions for the $f(x)$:

$$f(x) = f(x, \alpha, \beta, \gamma),$$

the α, β, γ being parameters which had to be chosen so as to make (11) a minimum.

Now, for incomplete shells the electron moment of momentum, $J \neq 0$, there exists space degeneracy, and $2J + 1$ linear independent states. Writing one of these as a single determinant, then the operator O will change it into a linear combination of determinants, which together contain more than n functions $f(x)$. This difficulty disappears in the case of completed shells. Here, without limiting the generality, we can make some simplifications.

(1) The functions $f(x)$ can be chosen to be orthogonal

$$(f_i, f_k) = \delta_{ik}. \quad (12)$$

This is readily proved in a geometrical way: ψ is a function of the points $x_1, \dots, x_n$, and is in fact, the determinant of the n vectors:

1. vector $f_1(x_1), f_1(x_2), \dots$
2. vector $f_2(x_1), f_2(x_2), \dots$
- $\vdots$

that is, ψ measures the *volume of their parallelepiped*. But this can be shifted into another one without *changing its volume*, by taking

$$f_1^* = f_1 \quad (13)$$

$$f_2^* = f_2 - \frac{(f_2, f_1)}{(f_1, f_1)} f_1$$

$$f_3^* = f_3 - \frac{(f_3, f_2)}{(f_2, f_2)} f_2 - \frac{(f_3, f_1)}{(f_1, f_1)} f_1,$$

$$\vdots$$

that is, by orthogonalising the set $f_n(x)$ in the well-known way. ψ is not altered by this process.

(2) The condition that $\psi(x_1, \dots, x_n)$ shall represent a ^1S -state of the atom, together with the condition (9) allows a further simplification. If ψ represents a ^1S -state, then it must be spherically symmetrical. Otherwise the states $O\psi \neq \psi$ would belong to the same eigenvalue and therefore would have to be space-degenerate, which contradicts the definition of a ^1S -state.

Theorem.—We assert now that *without altering* ψ , our set of functions $f_1, \dots, f_n$ can be transformed in such a way that the set splits up into several sets of the special form:

$$\left. \begin{array}{ll} 1 \text{ set: } g_{l_1}(r) Y_{l_1}^m & (m = -l_1, \dots, +l_1) \\ 2 \text{ set: } g_{l_2}(r) Y_{l_2}^m & (m = -l_2, \dots, +l_2) \\ \vdots & \end{array} \right\} \quad (14)$$

Here l_1 may be equal to l_2 but then necessarily $(g_{l_1}, g_{l_1}') = 0$ in order to make the product functions orthogonal.

According to this theorem, therefore, no further restriction of generality is implied by solving the variation problem (11) under the special assumption (14), which involves a much smaller number of unknown functions.

All this holds only for 1S-terms.

Proof.—Our proof is again chiefly geometrical. $\psi(x_1, \dots, x_n) = \text{Det.}(f_1, \dots, f_n)$ may be considered as the volume of the parallelepiped of the n vectors in n -dimensional space:

1. vector $p_1(x_1)$ with the components $f_1(x_1), \dots, f_n(x_1)$
2. vector $p_2(x_2)$ with the components $f_1(x_2), \dots, f_n(x_2)$.
- ⋮

To every point x in three-dimensional space belongs one vector in n -dimensional space. Altogether, we have, therefore, a three-dimensional vector field in n -dimensional space.

The rotation O may transform x into x'

$$Ox \rightarrow x'.$$

Then

$$Op(x) = p(Ox) = p(x') = p'. \quad (15)$$

A rotation O in three-dimensional space effects a transformation of the vector field into itself.

The group of rotations in ordinary space is isomorphic to the group of these vector transformations in n -dimensional space. *But these must be linear.* In fact, let us fix

$$x_1, \dots, x_{n-1}.$$

Their vectors are

$$p_1(x_1), \dots, p_{n-1}(x_{n-1}).$$

Then, let us vary p_n on a hyperplane at the distance a from the hyperplane $p_1, \dots, p_{n-1}$. The determinant of $p_1, \dots, p_n$ then remains constant. Now, the operator O may bring $p_1, \dots, p_{n-1}$ into $p'_1, \dots, p'_{n-1}$. Then, from $O\psi = \psi$, we conclude that p'_n lies on a hyperplane parallel to the hyperplane $p'_1, \dots, p'_{n-1}$. The transformation O is therefore such as to transform intersections of any hyperplane with the vector field into intersections of some other hyperplane with the vector field. But such a transformation must be a linear one. Our isomorphism gives, therefore, a representation of the group of rotations by linear transformations. Furthermore, the representation matrices $O_{rr'}$ have the determinant 1, as no parallelepiped of n vectors changes its volume.

And more, the matrix must be orthogonal, if $f_1, \dots, f_n$ were orthogonal since this property cannot be lost by rotation. Our representation must therefore be equivalent to a direct product of the well-known irreducible representations of the group of rotations :

$$O \text{ equivalent to } [D_{l_1} \times D_{l_2} \times \dots],$$

where the same l may or may not occur several times.

Now, by an orthogonal transformation we split up $f_1, \dots, f_n$ into groups :

$$\begin{aligned} f_{l_1}^m (m = -l_1, \dots, +l_1) \\ f_{l_2}^m (m = -l_2, \dots, +l_2), \\ \vdots \end{aligned}$$

so that

$$Of_l^m = \sum D_{mm'}^l f_l^{m'} \quad (16)$$

where $D_{mm'}^l$ are exactly the transformation matrices of the spherical harmonics. Let us now consider the set $f_{l_1}^m(r, \vartheta, \phi)$, ($m = -l_1, \dots, +l_1$) for $r = r_0$.

Here we have a set of $2l_1 + 1$ functions on the sphere, which transforms into itself under the group of rotations ; they form an irreducible invariant subspace of $2l_1 + 1$ dimensions of the Hilbert space of all functions on the sphere. But there exists only *one* such subspace, the one of the spherical harmonics of order l_1 . $f_{l_1}^m(r_0)$ must, therefore, be proportional to $Y_{l_1}^m(\vartheta, \phi)$:

$$f_{l_1}^m(r_0, \vartheta, \phi) = g_{l_1}(r_0) Y_{l_1}^m(\vartheta, \phi), \quad (17)$$

where $g_{l_1}(r_0)$ is the factor of proportionality. This is the result announced in the theorem.

We must add a few words about the spin. It is in accordance with the neglect of spin forces, that we take account of its existence only in so far as it alters the symmetry scheme. For a ^1S -state, we may therefore proceed by dividing our set of functions $f_1, \dots, f_n$ into

$$f_1^+, \dots, f_{n/2}^+ \quad \text{and} \quad f_1^-, \dots, f_{n/2}^-, \quad (18)$$

where the f represent functions of x, y, z only and the $+$ or $-$ sign signifies that $f = 1$ when $s = \frac{1}{2}$ or $s = -\frac{1}{2}$ and $f = 0$ otherwise. The state of the atom is described by the determinant of all n functions :

$$\psi = \text{Det. } (f_1^+, \dots, f_{n/2}^-).$$

Here ψ is a function of all spatial and spin co-ordinates of n electrons. If we consider ψ as a function of space co-ordinates only, for specified spin-values :

$$\begin{aligned} s_{i_1} = s_{i_2} = \dots = s_{i_{n/2}} &= +\frac{1}{2}, \\ s_{i_{n/2+1}} = \dots = s_{i_n} &= -\frac{1}{2}, \end{aligned}$$

then ψ becomes a product of two determinants :

$$\begin{aligned} \psi^*(x_1, y_1, z_1 \dots x_n, y_n, z_n) &= \text{Det. } [f_1(x_{i_1}), \dots, f_{n/2}(x_{i_{n/2}})] \\ &\times \text{Det. } [f_1(x_{i_{n/2+1}}), \dots, f_{n/2}(x_{i_n})]. \end{aligned} \quad (19)$$

For a ^1S term, each of these determinants must be spherically symmetrical, and the set $f_1, \dots, f_n$ must therefore split up into sets of the kind discussed before.

In the following paragraph, ψ means always the big determinant, with spin co-ordinates not fixed.

§ 3. The Interaction Energy of Atoms in ^1S States.

The calculation of the interaction energy can now be effected quite straightforwardly in the usual way :

1. *Notations.*—Suppose two atoms, nuclei A and B, have m and n electrons. Then, we have

μ functions $\alpha_1 \dots \alpha_\mu$, associated with A,

and

ν functions $\beta_1 \dots \beta_\nu$, associated with B,

which split up into l -groups of the type

$$\alpha = a_l(r_a) Y_l^m(\vartheta, \phi), \quad [m = -l, \dots, +l] \quad (20)$$

and

$$\beta = b_l(r_b) Y_l^m(\vartheta, \phi), \quad [m = -l, \dots, +l]. \quad (21)$$

where r_a, ϑ, ϕ in α refer to polar co-ordinates round the nucleus of A, and r_b, ϑ, ϕ in β refer to polar co-ordinates round the nucleus of B.

2. The function of zero-approximation is now

$$\psi = \text{Det. } (\alpha_1, \dots, \alpha_\mu, \beta_1, \dots, \beta_\nu). \quad (22)$$

The total energy, unperturbed plus perturbation

$$E = E_0 + \varepsilon = (\psi, H\psi)/(\psi, \psi), \quad (23)$$

where H is the Hamiltonian of the combined system. Development of the determinants in numerator and denominator splits this expression up into a sum of "exchange integrals" of different types :

(a) *One term* without any exchange; it represents the mutual potential energy of the cells α and β . The parts, which are independent of R , belong to E_0 , and the rest is just the electrostatic interaction of the charge distributions*

$$V^{AB} = 4 \sum_{i=1}^{\mu} \sum_{k=1}^{\nu} \iint \left[\frac{1}{r_{12}} + \frac{1}{R} - \frac{1}{r_{a1}} - \frac{1}{r_{b2}} \right] |\alpha_i(1)|^2 |\beta_k(2)|^2 d\tau_1 d\tau_2. \quad (24)$$

Here, the sums over i and k can be effected under the integral for each l -group separately,

$$\sum_m a_l^2(r) |Y_l^m(\vartheta, \phi)|^2 = (2l+1) a_l^2(r), \quad (25)$$

so that we may write as well

$$V^{AB} = 4 \sum_i \sum_{i'} (2l+1) (2l'+1) \iint \left[\frac{1}{r_{12}} + \frac{1}{R} - \frac{1}{r_{a1}} - \frac{1}{r_{b2}} \right] a_l^2(r_a) b_{l'}^2(r_b) d\tau_1 d\tau_2 \quad (26)$$

each of these double-integrals will be *negative* at great distances, as has been shown by the author in a previous paper.†

(b) Terms which correspond to an exchange of *one pair* of electrons

$$J^P = - \sum_{i=1}^{\mu} \sum_{k=1}^{\nu} \iint \left[\frac{1}{r_{12}} + \frac{1}{R} - \frac{1}{r_{a1}} - \frac{1}{r_{b2}} \right] \alpha_i(1) \bar{\alpha}_i(2) \beta_k(1) \bar{\beta}_k(2) d\tau_1 d\tau_2. \quad (27)$$

The integration refers to spatial and spin co-ordinates. Therefore only pairs with parallel spin give a non-vanishing contribution. Again, here we may carry out the sum for each l -group, using the results derived in paragraph 1:

$$\sum_m a_l(r_{a1}) a_l(r_{a2}) Y_l^m(1) \bar{Y}_l^m(2) = a_l(r_{a1}) a_l(r_{a2}) \cdot (2l+1) \cdot P_l(\cos 1 \hat{A} 2).$$

J_P results, therefore, as a sum of exchange terms, each of which refers to an exchange between two closed shells. A single one of these has the form:

$$J_{l,l'} = (2l+1) (2l'+1) \iint \left[\frac{1}{r_{12}} + \frac{1}{R} - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} \right] a_l(r_{a1}) a_l(r_{a2}) b_{l'}(r_{b1}) b_{l'}(r_{b2}) \\ \times P_l(\cos 1 \hat{A} 2) P_{l'}(\cos 1 \hat{B} 2) d\tau_1 d\tau_2.$$

They differ from the ones considered in previous papers only by the two Legendre polynomials P_l and $P_{l'}$. The effect of these may easily be predicted.

* The spin doubles the number of electrons in each cell and so gives rise to the factor 4.

† 'Ann. Physik.,' vol. 5, p. 36 (1930), Anhang 3, No. 2.

Heisenberg showed, that, for higher principle quantum numbers the product of the radial parts of the eigenfunctions has a marked maximum near the midplane of A and B making the term $1/r_{12}$ in the integral predominant, so that the whole integral becomes positive.

Now, for points 1 and 2 lying on the midplane near the axes AB, the angles $\widehat{1A2}$ and $\widehat{1B2}$ become acute. But in the first quadrant the first Legendre polynomials decrease monotonically, so that again smaller distances have a higher weight and the term $1/r_{12}$ becomes more and more predominant with increasing l and l' .

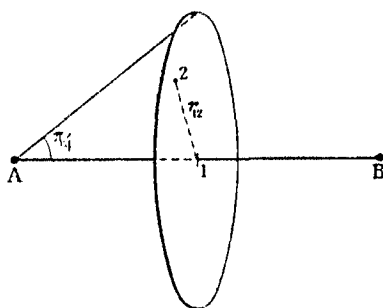


FIG. 1.

As an example to give a rough idea of the effect, we will evaluate the integrals for a simplified model :—

$$a_l(r_a) \cdot b_l(r_b)$$

unity on the circular disc indicated in the figure and zero everywhere else. The integrals are only taken over $d\tau_2$, the point 1 being fixed in the origin. Table I gives the results and the discussion.

Finally, we have—

(c) Terms which correspond to an exchange of two electron pairs, which can be omitted, owing to the approximate orthogonality of α and β .

(d) Terms which arise from the denominator in formula (23). They are of little influence at great distances.

Table I.—Exchange-integrals between Closed Shells.

$2l+1$ $2l'+1$		1	3	5	7	9
	l l'	0	1	2	3	4
1	0	1.000	0.882	0.678	0.445	0.241
		-0.750	-0.621	-0.405	-0.166	+0.026
		0.250	0.261	0.273	0.279	0.267
3	1		0.785	0.620	0.429	
			-0.520	-0.348	-0.165	
			0.265	0.272	0.264	
5	2			0.518		
				-0.250		
				0.268		

The table gives the numerical values of $J_{ll'}$ for a simplified model. In each square is the first number, the integral over $\frac{1}{r_{12}}$, the second number the integral over $\frac{1}{R} - \frac{1}{r_{a1}} - \frac{1}{r_{b1}}$. These numbers decrease with increasing l and l' owing to that $P_l < 1$. The third number is the sum of both, which turns out to be nearly constant.

This has to be multiplied by $2\pi(2l+1)(2l'+1)$ in order to give $J_{ll'}$. One sees at once how $J_{ll'}$ increases with increasing l and l' .

Summary.

1. The problem of the best representation of an atom with n electrons in a ^1S state by a determinant of n independent functions can be reduced in a unique way to the determination of a much smaller number of independent functions.

2. The electrostatic as well as the exchange-energy of two rare gas atoms can be written as a sum, the terms of which correspond to the interaction of pairs of completed shells.

3. The electrostatic energy will always be negative for great distances.

4. The exchange energy* tends to negative values for increasing azimuthal quantum numbers.

* The exchange-energy is the negative sum of all exchange-integrals; these latter tend to positive values. See formula (27).

5. The attractive field of the higher rare gas atoms is probably due to the first order perturbation, rather than to polarisation.

The author wishes to express his thanks to Dr. C. Zener for helpful discussions on the subjects treated in § 2, and to Prof. Lennard-Jones for his kind interest in the progress of the work and his help in the preparation of the paper for publication.

OBITUARY NOTICES.

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T. J. F.A. BROMWICH.

THOMAS JOHN L'ANSON BROMWICH, 1875-1929.

THOMAS JOHN L'ANSON BROMWICH, who died on August 24, 1929, was one of the most accomplished and most versatile among English mathematicians of the last fifty years. He was born in Wolverhampton on February 8, 1875, but spent his youth in Natal, and was educated in Durban. He came to Cambridge, as a Pensioner of St. John's College, in October, 1892. A brilliant career as an undergraduate ended when he was Senior Wrangler in 1895, in an exceptionally strong year which included also E. T. Whittaker and J. H. Grace. He obtained a Fellowship in 1897, but left Cambridge in 1902 to be Professor of Mathematics in Galway, returning in 1907 when appointed a permanent lecturer at St. John's. He was also a University Lecturer from 1909 to 1926. He became a Fellow of the Royal Society in 1906 and a Doctor of Science in 1909. He was for many years a most enthusiastic and energetic member of the London Mathematical Society, of which he was Secretary from 1911 to 1919, and Vice-President in 1919 and 1920. He married in 1901, and leaves a widow and one son.

Bromwich's work covers so wide a field that it is hardly possible for any one person to deal with it competently. His later work in mathematical physics is discussed in Dr. Jeffreys' notice in the 'Journal of the London Mathematical Society,' vol. 5, p. 220. Prof. H. W. Turnbull and Prof. A. E. H. Love have very kindly provided me with notes concerning Bromwich's early work, in algebra and in applied mathematics respectively, and what I say about these subjects is very largely based on them.

Bromwich was the author of one large treatise, "An introduction to the theory of infinite series" (Macmillan, 1908), a second edition of which appeared in 1926; of one of the Cambridge Tracts, "Quadratic forms and their classification by means of invariant-factors" (1906), long out of print; and of from seventy to eighty papers in mathematical and physical journals. It is noteworthy that over fifty of these papers had appeared by the end of 1906, and that after 1908 he published comparatively little of importance, except for the work on "normal co-ordinates" and the operational calculus which was his primary interest in his later years of activity. After the war he was never in normal health, but his period of greatest fertility had ended a good many years before. There is no doubt that he had for long been overworked. He was engaged in original work in several different fields; he put a great deal of energy into his college and university lectures, where his passion for working out every point in detail must have added enormously to his labours; and to all this he added a considerable amount of examining and private coaching. The best pure mathe-

matician among the applied mathematicians of Cambridge, and the best applied mathematician among the pure mathematicians, he must have been an ideal coach for a Tripos candidate of sufficient strength, and if there could have been a *dons'* Tripos, we would all have laid odds on him to be first; but the cost of all this was heavy both for mathematics and for Bromwich himself, and he never quite fulfilled his early promise. He would have had a happier life, and been a greater mathematician, if his mind had worked with less precision. As it was, even the best of his work is a little wanting in imagination. For mastery of technique in a wide variety of subjects, it would be difficult to find his superior, but he lacked the power of "thinking vaguely."

Bromwich plunged enthusiastically into research immediately after taking his degree. He was, in the first instance, an applied mathematician; his special subjects in Part II of the Tripos had been Hydrodynamics, Elasticity, Optics, and Electricity and Magnetism. He was, however, an applied mathematician of an extremely "analytical" type. He had no physical training, and does not in his early work at any rate show any very great interest in physics for its own sake. He does not seem really to care much about the physical world or the light which his analysis may throw on it, but rather to regard the world as created to illustrate his analysis. What he always wanted was the correct answer to the physical question when reduced to a problem of analysis, a convincing proof, and a logical presentation. It is only fair to add that in his later years, when applied mathematics became again the principal object of his thoughts, he showed a good deal more of the spirit of a genuine physicist than ever before.

The result of this was that Bromwich soon found himself engaged primarily in pure mathematical research. He began, no doubt, by finding a good deal of the current physics deficient in accuracy and in technique, and set himself to remedy some of the deficiencies. This made him, first an algebraist, and then an "analyst" in the technical sense. As soon as he began to study analysis seriously he found, as well he might, that the teaching of analysis in England, in Cambridge and elsewhere, was slovenly and incompetent, and he set to work with characteristic energy to improve it. This was the period of his "Infinite series," when he was in the first place an analyst, more from force of circumstances than from any spiritual necessity. It was, however, with algebra that he occupied himself first, and I must begin by saying something about his work in this field, which he abandoned altogether later.

Bromwich's most important contributions to algebra are to be found in his Tract and in the papers 4, 6, 8, 17, 22, and 24*. The most striking of these papers to the ordinary reader is certainly 22, and the result is easily stated and stands apart from the rest of his work, though the proof depends on theorems first proved explicitly by Bromwich himself in 6, 8, and 23. The

* See the references at the end of the notice.

problem is the old problem of finding bounds for the real and imaginary parts of the roots of the characteristic equation of a linear substitution. If the substitution is

$$(A) \quad \xi_s = \sum_r a_{sr} x_r \quad (r, s = 1, 2, \dots, n),$$

then the equation is

$$|A - \lambda E| \equiv \begin{vmatrix} a_{11} - \lambda & a_{12} & \dots \\ a_{21} & a_{22} - \lambda & \dots \\ \dots & \dots & \dots \end{vmatrix} = 0,$$

where $|A|$ is the matrix of A and $|E|$ is the unit matrix. The classical results are as follows. The roots are all real when A is real and symmetrical (Cauchy, 1829), or, more generally, when A is Hermitian, *i.e.*, when a_{rs} and a_{sr} are conjugate (Christoffel, 1864). They have unit modulus when A is real and orthogonal (Brioschi, 1854). Finally, they are pure imaginaries when A is real and alternate, *i.e.* when $a_{rs} = -a_{sr}$ (Weierstrass, 1879). The general case was considered first by Bendixson (1900) and Hirsch (1902), by the former for real and by the latter for complex A . Bromwich, using a different method, completes their results and arrives at a final theorem. Suppose that $\lambda = \mu + i\nu$ is a root and write

$$b_{rs} = \frac{1}{2} (a_{rs} + \bar{a}_{sr}), \quad b_{sr} = \frac{1}{2} (a_{sr} + \bar{a}_{rs}), \\ ic_{rs} = \frac{1}{2} (a_{rs} - \bar{a}_{sr}), \quad ic_{sr} = \frac{1}{2} (a_{sr} - \bar{a}_{rs}),$$

where the bar denotes the conjugate, so that $|B|$ and $|C|$ are Hermitian. Then, after Christoffel, the roots of $|B - \lambda E| = 0$ and $|C - \lambda E| = 0$ are real, say $\mu_1^*, \mu_2^*, \dots$, and $\nu_1^*, \nu_2^*, \dots$, respectively; and Bromwich's theorem is that μ lies between the least and the greatest of the μ^* and ν between the least and the greatest of the ν^* .

The content of the other algebraical papers is more difficult to characterise. They are not at all easy to read, for Bromwich shows defects as an expositor which he never wholly overcame. He is clear enough in detail, but, as Berry said very justly later, in a review of his "Infinite series," he does not help the reader by laying emphasis at the right moment on the really fundamental idea. His first object in all this work is to expound and extend the ideas and methods of Kronecker in the theory of quadratic and bilinear forms, which he was the first to introduce to English readers. Yet one will search in vain for any quite clear and explicit statement of the fundamental difference between Kronecker's methods and those of writers before him.

The difference shows itself particularly clearly in the very simplest case, that of the reduction of a single quadratic form

$$A(x_1, x_2, \dots, x_n) = \sum a_{rs} x_r x_s$$

to a sum of squares. Lagrange and Kronecker each reduce step by step, making

$$A(x_1, x_2, \dots, x_n) = c\xi_1^2 + B(\xi_2, \xi_3, \dots, \xi_n),$$

to take the simplest case. In Lagrange's reduction $\xi_2, \xi_3, \dots$ are $x_2, x_3, \dots$; the coefficients in B have changed but not the variables. In Kronecker's, $B = \sum a_{rs} \xi_r \xi_s$, the coefficients are the same but the variables have changed†. This divergence of procedure naturally persists and widens throughout the whole theory which Bromwich is occupied in developing.

In detail Bromwich's work is impressive, and his contributions to the theory substantial. In 4 he considers the reduction of the linear substitution A to a "canonical" substitution‡, by a method similar to that of Netto. In 5 he begins by considering the corresponding problem for the more general system

$$\sum_r b_{sr} \xi_r = \sum_r a_{sr} x_r, \quad (r, s = 1, 2, \dots, n),$$

with special reference to the "singular" case in which $|A - \lambda B| = 0$ for all λ . Then, after a dynamical application, he passes to the central problem of the theory, that of the simultaneous reduction of the two bilinear forms

$$A(x, y) = \sum a_{rs} x_r y_s, \quad B(x, y) = \sum b_{rs} x_r y_s.$$

It is familiar that a single bilinear form A of "rank" p is reducible to the form

$$A^* = X_1 Y_1 + X_2 Y_2 + \dots + X_p Y_p$$

by an infinity of substitutions $x = PX, y = QY$. The most interesting case is that in which the substitution is "congruent," i.e. when the form of the substitutions for X and Y is the same. The necessary and sufficient condition that A should be reducible to A^* by a congruent substitution is that A should be symmetric. An alternate form may be reduced by such a substitution to§

$$X_1 Y_2 - X_2 Y_1 + X_3 Y_4 - X_4 Y_3 + \dots$$

Kronecker gave a general process for the congruent reduction of any A , which Bromwich, in 23, works out for symmetric and alternate forms.

The next problem is that of two forms A, B , or a "Schaar" $A - \lambda B$. If $|B| \neq 0$, then $A - \lambda B$ can be reduced to

$$C(X, Y) - \lambda(X_1 Y_1 + X_2 Y_2 + \dots + X_n Y_n),$$

where C is a sum of forms like||

$$aX_1 Y_1 + (aX_2 + X_1) Y_2 + \dots + (aX_r + X_{r-1}) Y_r.$$

† See Bôcher's "Introduction to higher algebra," 181.

‡ See Hilton's "Linear substitutions," 29.

§ For all these theorems, see Hilton, 69, 73, 75.

|| Hilton, 173.

Thus, in the simple case when the roots of $|A - \lambda B| = 0$ are distinct, there are n such forms each consisting of the first term only. The general problem has been attacked by many writers. In 5, Bromwich gives a method of his own, again paying special attention to the singular case when $|A - \lambda B| \equiv 0$, and illustrating it on Darboux's example

$$\begin{aligned} A &= a_1 (x_1 y_1 + \dots + x_{n-1} y_{n-1}) + x_2 y_1 + \dots + x_n y_{n-1}, \\ B &= x_1 y_1 + \dots + x_{n-1} y_{n-1}. \end{aligned}$$

In all this there is no question of congruent reduction, a special problem which Bromwich considers in 6 and 23. Kronecker gave a process for the congruent reduction of two quadratic forms, and Bromwich, in 20, applies this method to the four cases in which each form is symmetric or alternate, and also works out the reduction of a pair of Hermitian forms by conjugate substitutions.

In his Tract (and in 17, which is practically a sketch for it), Bromwich confines himself to *quadratic* forms, again using Kronecker's methods. He does not follow Kronecker at all slavishly, and, indeed, the very friendly critic (W. F. Meyer) in the "Jahrbuch" takes him to task for his neglect of Kronecker's rational invariants. In many ways the Tract is exceptionally clear and illuminating, especially for readers who like general processes illustrated by particular applications at every stage, and it has been widely read and quoted while his more general work has been neglected. The geometrical illustrations are very full and clear; there is a complete statement on pages 46-47 of the results for two quadratics in four variables, in terms of the geometry of quadrics; and the applications in the last chapter include, besides the obvious applications to the metrical classification of quadrics (in point or line co-ordinates), applications to bicircular quartics, to cyclides, to quadratic line complexes, and to dynamics. This richness in detail, within the narrow limits of a Tract, may well excuse some neglect of certain sides of the theory.

It was perhaps as an algebraist that Bromwich showed the highest natural talent, but it is no doubt as an analyst, as the author of "Infinite series," that he is most widely known. This book, and the various investigations into which he was led when writing it, must have occupied the principal energies of a good many years of his life.

It is to misjudge Bromwich to imagine him an "analyst" in the fullest sense of the word. He was a very able analyst, but an analyst made and not born. He was no *Funktionentheoretiker*. He knew the theory of series extremely well, and the theory of functions very well up to a point, but there both his knowledge and his inclination stopped short rather abruptly, and none of his work shows any interest in the most modern developments of the theory of functions either on the real or the complex side. No one will blame for that a man whose fault was to be interested in too many things rather than too few.

The book is unquestionably a very fine one. It is not merely a good and an interesting book; it has a character and a distinction which show at once that it is written by an exceptional mathematician. It is easy to criticise it, and many people have done so. It is excellent in detail; there are singularly few actual mistakes, when the richness of the content is considered, and it is easy to find a clear and convincing proof of any particular theorem; but the general plan of the book is open to obvious objections, and, considered as a reasoned and comprehensive text-book, it is not so satisfactory as Knopp's. There is a clear and temperate statement of these objections in the review by Berry which I have already quoted. The continual forward references to the elaborate appendices are, as Berry points out, very trying, confusing to a student and irritating to an expert; the arrangement suggests that Bromwich "originally intended to confine himself almost entirely to series and to use only the elements of the infinitesimal calculus, but that in the course of writing he became interested in the allied theories of definite integrals, and added his Appendix III rather as an afterthought." One might add that it is really impossible to justify the position and arrangement of Appendix I; part of it should come at the beginning, and the rest should be split up and incorporated in different chapters. It is also very difficult to defend the logical attitude adopted by Bromwich towards the elementary transcendental functions. To use the properties of logarithms from the beginning, justifying their use later by methods based on the integral calculus, may perhaps be defensible in an elementary course of analysis, but not in a systematic treatise on the theory of infinite series. "Algebraical analysis" as such has a right, in a book like this, to a more serious treatment.

It would be unfair to lay too much stress on these undeniable defects, in view of the great and striking merits of the book. It has two supreme merits, rare indeed in English text-books of its time; it is thoroughly interesting, and the detailed analysis is almost always sound and clear. Whatever one may think of the general scheme, individual sections are hardly ever obscure. Finally, among all treatises on infinite series, this book stands by itself as a work of reference and a storehouse of information; it really is "a book that no mathematician can do without."

One particular merit is that, when Bromwich has to prove a rather difficult theorem, he is so careful to separate any general difficulty of principle from the small complications due to the special functions considered. A very good example of this is his treatment of the product for $\sin x$. The difficulties of principle are disposed of by a general theorem ("Tannery's theorem" of § 49), and all that remains is to verify that the conditions are satisfied in the special case. In such proofs as those in Hobson's "Trigonometry" or Chrystal's "Algebra" the two sources of trouble are encountered simultaneously, with the result of a much heavier strain on the comprehension of a moderate student.

The best chapters have always seemed to me to be Ch. 5, on double series, and Ch. 11, on divergent and asymptotic series. In each case Bromwich was practically introducing the subject to English readers. Ch. 5 is quite short, but it contains all the essentials and is admirably clear. The examples are most instructive, and it cannot be said here, as it can in some parts of the book, that they are so numerous and so difficult that they overshadow the general theory.

Ch. 11 must be judged by a different standard. The subject matter of Ch. 5 was already almost "classical," and there would be no reason even now for any very substantial change; while Ch. 11 is essentially a "pioneer" account of a theory which has changed almost out of recognition since. It would be difficult now, for example, to justify the proportion of space allotted to Borel's method, while the account of the "Cesàro" methods is obviously inadequate. For these reasons much of this chapter has been struck out of the second edition, a decision which is perhaps correct, but which takes away a good deal from the attractiveness of the book.

The book contains the results of a great deal of original research, especially of the papers which Bromwich published in the 'Proceedings of the London Mathematical Society' from 1903 to 1908. Large parts of these papers are incorporated in the text, the appendices, or the examples, and give the book a refreshing air of liveliness and actuality. If we contrast it, for example, with Chrystal's "Algebra," there can be no doubt that it is incomparably a better book. There are many directions in which it has suggested problems for further research. Thus in Ch. 11 Bromwich raises for the first time the problem of the relations between Borel's and Euler's methods of summation; it was not till 1922 that Knopp and Rademacher gave a definite solution.* What Bromwich actually proved was very little, but it is only one of many cases in which his book initiated a very interesting discussion.

I may add a few remarks about one or two of Bromwich's individual contributions to analysis. They begin with 11, in which he makes a remark of considerable importance in the theory of double and repeated limits. The question is that of the equality of the limits

$$\lim_{x \rightarrow 0} \lim_{y \rightarrow 0} f(x, y), \quad \lim_{y \rightarrow 0} \lim_{x \rightarrow 0} f(x, y): \quad (1)$$

let us denote the inner (simple) limits, which we assume to exist, by $g(x)$ and $h(y)$ respectively. "It is the merit of Bromwich," says W. H. Young,† "to have recognized the importance" of the equation

$$\lim_{y \rightarrow 0} \lim_{x \rightarrow 0} \{f(x, y) - g(x)\} = 0 \quad (2)$$

* See Knopp, 'Math. Zeitschrift,' 15 (1922), 238-242. Actually the region of Borel summability includes that of Euler summability (as is suggested by Bromwich's examples), and is the limit of the region covered by iteration of Euler's method.

† 'Trans. Camb. Phil. Soc.', 21 (1910), 368.

in this problem. It is evident that (2) is true whenever the limits (1) exist and are equal. What is less obvious is that (2) implies the existence of the limits (1) and not merely their equality when they exist. Bromwich makes a number of interesting applications of this principle.

Another paper on double limits is 12, about the extension of Abel's continuity theorem to power series in several variables. This is a joint paper, but I am concerned here only with a remark which is Bromwich's, and which illustrates his quickness in seeing curious connections between pure and applied mathematics. The force between two equal electrified spheres of radius a , in contact and at potential V , is $V^2(\frac{1}{2} \log 2 - \frac{1}{2})$. This result was found by Kelvin; Bromwich gives a direct proof in 19. Kelvin, however, uses the method of images, which leads to the series

$$V^2 \sum \sum (-1)^{i+j} \frac{ij}{(i+j)^2},$$

a series which is obviously not convergent as a double series, and does not even converge when summed by squares, though the *repeated* series are convergent and have the value which Kelvin finds. The method of images, in short, fails; it is not true that the force between the spheres is "the force between the two sets of images," which could only be regarded as the limit of the sum over a square.

I mention, in passing, the very interesting papers 13 and 14. The first concerns the theory of the logarithmic potential, and reveals some curious contrasts with Petrini's results for the Newtonian case. In the second Bromwich studies the analogues for series of zonal harmonics of Abel's continuity theorem (a field in which it seems that there is still something to be done). Another important paper on a similar topic is 24, in which Bromwich considers the limit

$$\lim_{x \rightarrow 0} \sum a_n v_n(x),$$

where $v_n(x) \rightarrow 1$ for every n , and $\sum a_n$ is a divergent series summable by Cesàro's or Hölder's means. The results which he obtains have been mostly superseded by more comprehensive theorems, but the paper played a considerable part in its time in the development of the theory of divergent series; it is here, for example, that we first find an explicit statement of the critical condition

$$\sum n^k |\Delta^{k+1} v_n| < K.$$

It seems odd now that so skilful an algebraist as Bromwich should not have been able to prove the general equivalence of the two kinds of means, but there is a great deal in the theory of series which seems easy now and seemed very difficult in 1903.

It remains to say something about Bromwich's earlier work in applied

mathematics. His first published paper was 1, on a subject suggested by Larmor. This paper has become a classic. Later Bromwich found his own subjects, though he often makes it clear that they have been suggested by the work of others. Thus 3 was suggested by a paper of Forsyth, and Bromwich's interest in Forsyth's work arose from a passage in Darboux's chapters on minimal surfaces, referred to in 2. The last paper contains the elegant theorem that a surface defined by a tangential equation $p = p(l, m, n)$, where p is homogeneous and of degree one, is minimal where $\nabla^2 p = 0$.* This was one of Bromwich's occasional contributions to geometry. There are others in 7, which contains a new proof and generalizations of Liouville's theorem concerning conformal space-transformations, and in 18, a joint paper with Hudson, in which there is a very clear account of some of the more delicate points in the theory of envelopes, and a number of results concerning osculating envelopes difficult to find elsewhere. But Bromwich would never have pretended to be a "geometer" in any very real sense of that difficult word.

Other early papers, such as 9 and 10, are concerned with physical applications of his algebraical work. Bromwich, when a student, worked out for himself simple methods of finding the wave surface in a medium from the general equations of electricity or electrodynamics. A note on this subject by Macdonald appeared in Vol. 32 of the 'Proceedings of the London Mathematical Society,' and Bromwich, having acquired a wide knowledge of algebra in the interval, was in a position to construct, in 10, a much more comprehensive theory.

Another development of his early work on the electromagnetic field is shown in 21 and 16. Bromwich had found a new solution of the general equations as early as 1899, when there was a good deal of discussion of the theory of scattering by a spherical obstacle. This was first published partially as a Tripos question in 1910, and then much later in 21; its value as a means of investigation is exhibited more fully in 16.

15 is another very interesting and valuable paper in which Bromwich returned in later years to his work as a student. He had already published one paper (20) on the determination of the potential of a symmetrical distribution from its values on the axis of symmetry. He returns to this problem in 15, and finds a new solution

$$X_n = r^n P_n(\mu) \log \frac{r+z}{2a} - 2r^n \left\{ \frac{2n-1}{1 \cdot 2n} P_{n-1} \right. \\ \left. - \frac{2n-3}{2(2n-1)} P_{n-2} \dots + \frac{(-1)^{n-1}}{n(n+1)} \right\}$$

* The theorem was discovered independently by Richmond. See H. W. Richmond, 'Trans. Camb. Phil. Soc.' 18 (1899), 324-332, where the idea is applied more systematically to the theory of minimal surfaces.

of Laplace's equation with an axis of symmetry, and applies it to determine potentials of circular discs of variable density. A more obvious form of the solution, viz.

$$X_n = a^n \frac{\partial}{\partial n} \left\{ \left(\frac{r}{a} \right)^n P_n(\mu) \right\} - 2r^n P_n(\mu) \left(1 - \frac{1}{2} + \frac{1}{3} - \dots - \frac{1}{2n} \right),$$

was pointed out afterwards by Watson.

It is, no doubt, on Bromwich's later work, which is dealt with by Dr. Jeffreys, that our judgment of him as a mathematical physicist must primarily depend. His earlier work reveals him not as a physicist but as a very powerful and accomplished mathematician, always on the watch for any application of his analysis to physics, and ready to turn it in almost any direction with singular quickness and versatility. However we may judge him as a physicist, or as a pure mathematician of any particular stamp, there can be no doubt about the substance and the distinction of his contributions to mathematics as a whole. We may feel that a mathematician of Bromwich's powers should have done more than he did, but what he did is a great deal more than the performance of any ordinary man, and it would be very hard to find anyone among his contemporaries who did so many things so well.

G. H. H.

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K. J. P. ORTON.

KENNEDY JOSEPH PREVITÉ ORTON, 1872-1930.

KENNEDY JOSEPH PREVITÉ ORTON was born at St. Leonards-on-Sea on January 21st, 1872, the eldest son of the late Rev. W. P. Orton.

He was educated first at Kibworth Grammar School, 1882-1885, and then at Wyggeston School, Leicester, 1885-1888. He entered St. Thomas's Hospital in 1889 and there was attracted to the study of chemistry by Bernays, then lecturer in the Medical School. He proceeded to Cambridge in 1891, having gained an exhibition at St. John's College, where his father had been a Foundation Scholar and a Wrangler. On taking a first class in the first part of the Natural Science Tripos of 1893, and gaining a Major Scholarship, he finally abandoned medicine for chemistry. After working under Professor Liveing and Dr. Ruhemann and taking the second part of the Tripos in 1895, he went with a Hutchinson Studentship to Heidelberg, where he worked under Victor Meyer and Auwers, and in 1896 obtained the Ph.D. "summa cum laude," a coveted distinction which in chemistry had never before at Heidelberg been gained by an Englishman.

After a year's research under Ramsay at University College, London, he became in 1897 senior Demonstrator in Chemistry at St. Bartholomew's Hospital and was promoted assistant lecturer in 1903. The same year he was appointed Professor of Chemistry in the University College of North Wales at Bangor, a position which he filled till his death. In this chair he succeeded Dobbie, who had held it since the foundation of the college and had built up there a strong school of chemistry.

From the time of his appointment he took a prominent part not only in the administration of Bangor College but in the work of the University of Wales as a whole. For several years he represented his college on the University Court, for many years he was a member of the University Senate, and on the reconstruction of the University was elected as the representative of his College Faculty of Science on the Academic Board, where he served from 1920-1927.

He was for a long period Dean of the Faculty of Science and at the time of his death was Vice-Principal of the college, a member of the University Faculty of Rural Science and of the Joint Academic Committee. He was an original member of the Appointments Board for Wales and took a marked interest in its development.

He was a member of the Council for the Preservation of Rural Wales and was always active in the endeavour to keep unspoilt all places of natural beauty or antiquarian interest.

He served twice on the Council of the Chemical Society from 1913-1917 and

1926-1929 and on the Council of the Institute of Chemistry from 1908-1911. He was elected a Fellow of the Royal Society in 1921.

He married in 1897, Annie, daughter of the Rev. W. Clement Ley, who survives him, with a son and two daughters.

Orton made the Bangor laboratory an even more active centre of chemical research than it had been under his distinguished predecessor. From it there issued year after year a steady flow of important work. He had been scarcely a year in Bangor when his attention was arrested by Dr. Greenley's geological maps of Anglesey. He was struck by the wealth of rock-types they exhibit, and by the fact that the origin of many of them was still unknown, and saw that for the solution of these problems it was essential to ascertain their chemical composition. He accordingly proposed to Dr. Greenley, and with his concurrence organised, a systematic campaign of analysis. This work threw considerable light on a number of geological problems, the most important being that of the origin of the celebrated glaucophaneschist, a beautiful rock known to occur in very few places in the world, but developed largely in Anglesey.

His most important researches however were concerned with substitution in aromatic compounds and the migration of atoms. He was introduced to this part of the science during his period at St. Bartholomew's Hospital and turned again and again to it and related subjects during his subsequent work, which led him to the conclusion that the migration of halogen in substituted acyl-anilides is dependent on the liberation of chlorine. From this conclusion he developed a method for the regulated chlorination of aromatic substances and for the production of an acetic acid solution of known chlorine concentration.

In collaboration with his students he carried out much valuable work on the mechanism of organic reactions and on the very interesting action of nitric acid upon unsaturated hydrocarbons.

He consistently applied physico-chemical methods to the elucidation of organic reactions and in some of his later work turned to the more purely physical side of the science.

Many of his students now hold educational and industrial positions of importance and two are professors of chemistry in the sister colleges of Cardiff and Swansea.

Orton, however, was much more than a chemist, and any survey of his activities which regarded this side of his life's work only would present a very one-sided view of his character.

He was in his right place as head of a department and a laboratory, where he was not only an excellent teacher, but a wise adviser and helpful friend to his students. His judgment and insight were rarely at fault. He would take infinite pains to give his students a good start in life and would help them long after they had left his immediate care.

His most marked characteristics were an intense vitality and vigour and a

deeply felt appreciation of the grander phenomena of the outside world, the changing sky, the piled thunder clouds, the path of the mountain storm. In this love of nature he was encouraged by his future father-in-law, who was one of the most original of meteorologists. The mountains and the coast near which his lot was cast were to him an ever present inspiration and delight and his friends came into closest contact with him and like to remember him best in the companionship of climbing or walks along the cliffs and seashore.

His lifelong and outstanding interest and pleasure was the observation and study of birds and of the hawks especially. He was a member of the British Ornithological Union, an honour of which he always expressed himself as very proud. Although he wrote little on this subject beyond occasional short articles on bird life in the weeklies and magazines, he left behind a large number of records of bird observations intended to form the material of a volume. With the help of one or two younger friends whom he had trained in field observation it is hoped that this may be published later.

Principal Emrys Evans writes of him, "As a member of the Climbers' Club he was an enthusiastic mountaineer, though he had followed his favourite pursuit less actively in recent years. He had an intimate acquaintance with the Snowdonian hinterland of Bangor, and it was characteristic of this avid observer of nature that he had combined with his mountaineering and his later motoring a cumulative study of the bird-life of mountain and moorland. It was once his frequent practice after his day's work to set off in the evening to some lonely farmhouse in the mountains, where he would spend the night, and rise before dawn to climb within observing distance of a raven's or a buzzard's precarious eyrie. His contributions on the "Birds of Llyn Ogwen" to Archer Thomson's "Climbing in the Ogwen District," and on "Bird Life in the Mountains" to Carr and Lister's "Snowdonia," show his intimate mastery of the subject, but most of his precious knowledge inevitably goes with him. In recent years his car bore him to the marshes and coasts of Anglesey and Llyn, and none who ever shared his journeys will forget the eager, almost boyish, enthusiasm with which his expert eye recognised his birds, or the zest which he brought to observing everything around him—the beauty of the countryside, the signs of the weather, the encroachments of quarry and human habitations, the remains of antiquity.

"He was not a narrow scientist. No University teacher was more ready to do battle for the humanities. He loved music, and was a regular attendant at the weekly college concerts. He would often rally to support the claims of the classics in Senate and committee if they seemed to be overlooked. It was in accordance with his broad, sympathetic outlook that he set himself to understand the Welsh people among whom he lived, whether they were the students of the college or the farmers and peasants of Caernarvonshire and Anglesey, and the generous insight which enabled him often to divine in them latent

qualities and possibilities led to an optimistic faith that inspired many of those who worked with him and under him. He lived intensely, and possessed withal a youthful buoyancy of spirit, an eager interest in men and things, a generous impulse which shrank from severe condemnations—qualities that invested his manifold activities with a certain æsthetic charm and completeness which those who were admitted into his fellowship will preserve in memory as a precious experience."

His brother writes : " He was an observer of unusual accuracy and delicacy. Nothing escaped his notice, and what he saw or heard was at once registered and grouped in his mind and acted upon with a swift and just decision when the time came. This was rendered easier by the simplicity and directness of his own nature. Hazy complexes and tortuous eddies were foreign to him. His mind moved on a free balance, like the hawk's flight he loved to watch, and his perception of external things was not blurred or shaken by internal twists and wrenches. His character was not only built on simple and harmonious lines ; its elements were of the finer clays—strong and durable affections, a severe sense of duty, loyal friendships, a generous quite unsentimental sympathy, and exceptional unselfishness which led him to a continuous beneficent activity, whether he was giving his best in graver matters, or a lift in his car to an old market-woman with her overweighted basket."

The vigour and freshness of mind which were his predominant characteristics seemed to promise a long life, but in the early part of this year his many activities had so seriously overtaxed him that an attack of pneumonia found him with no reserve of strength to resist it, and after a few days' illness he died, peaceful and acquiescent on March 16th.

He rests, according to his own expressed desire, in the beautiful churchyard of Llanfairpwll, overlooking the Menai Straits and the great mountain masses he loved so well.

F. D. C.



Amjan Bep

THE EARL OF BALFOUR—1848-1930.

ANY attempt to summarise Lord Balfour's public career would be out of place in these 'Proceedings.' It has been thought suitable, however, to include a short memoir dwelling on his early history and mental development, on his scientific and philosophical thought, and on his administrative work for scientific, industrial and medical research.

Arthur James Balfour was the son of James Maitland Balfour of Whittingehame, Haddingtonshire (died 1856), and of Lady Blanche Gascoyne Cecil, second daughter of the second Marquess of Salisbury. The father was a country gentleman of fortune and of some ability, but in no sense a philosopher or a thinker, or even a reader. He served in Parliament, organised a regiment of yeomanry and was chairman of the North British Railway. His career however, was cut off at an early stage by consumption. The mother, Lady Blanche Balfour, came of an able stock. Although the influence of the great Lord Burghley must be considered to have been long since exhausted, the abilities of that branch of the Cecil family had been recently recuperated by two marriages: the first with Lady Mary Amelia Hill, first Marchioness of Salisbury; and the second with Frances Mary, daughter of Bamber Gascoyne, and mother of the third Marquess, Prime Minister to Queen Victoria, and of Lady Blanche Balfour. Lady Blanche shared to a marked extent her brother's ability. She directed the education of her children, and found means of stimulating their intellectual interests, with the greatest tact and judgment. She was particularly judicious in the choice of the books which she read to them. On occasion she would cut out passages which were tedious or unsuitable, and substitute connecting links rewritten by herself.

Her lessons in arithmetic are remembered for the clear way in which the subject was presented. The reasons for the operation of "carrying," *e.g.* were lucidly explained, in contrast to the usual dogmatic method.

Although Lady Blanche's own tastes were literary rather than scientific, she successfully directed the attention of her children to various branches of natural history, and, in the case of some of them, the interests thus aroused bore no inconsiderable fruit. Thus Gerald and Francis Balfour wrote an account of the local geology of East Lothian, which has permanent value as a contribution to the subject. Francis Balfour, it is hardly necessary to remind the reader, eventually became Professor of Animal Morphology at Cambridge, a chair specially created for him. Those best qualified to judge held that his early death represented an irreparable loss to science.* His

* It has sometimes been imagined that Arthur Balfour derived his knowledge of science and his interest in it at second hand from his brother Frank. I am sure that no one with inside knowledge would share this view. The taste was innate in both of them, and came out in both, though in widely different forms.

youngest sister, Alice Balfour, assisted him to some extent in his studies, and has ardently continued the pursuit of local entomology up to the present. Arthur Balfour's eldest sister had a distinct gift for mathematics and physics, and in later years was able to render valued assistance to her brother-in-law, Lord Rayleigh, during his tenure of the Cavendish Professorship of Experimental Physics at Cambridge. She appears as joint author of some of his papers on Absolute Electrical Measurements.

It will be seen then that there was a marked scientific tone in the family of which Balfour was a member. The same was traceable in his uncle, Lord Salisbury, who to some extent occupied his leisure with botanising, and with experiments in electricity and magnetism, which he carried on in a private laboratory at Hatfield. Balfour seems to have taken less part than some of the others in these natural history studies. He had, for instance, no inclination for the hard work of a systematic search for fossils. But, no doubt, what was going on had its influence upon him.

In later life he took some practical interest in forestry on his estate, but he had no knowledge of horticulture, and no eye for bird life. On one occasion, well remembered in the family, he remarked that he had been disturbed by a bird which had got into his study. His youngest sister, alive with the instincts of a naturalist, wished to know what species it belonged to. But the only description he could give was "Oh, I don't know; average small bird." Although he had not this kind of knowledge himself, he respected it in others. As a young man, he had shooting, deer stalking and salmon fishing at his disposal, but he soon abandoned them in favour of lawn tennis and golf.*

Balfour first went to school at the Rev. C. G. Chittenden's at Hoddesdon. His opinion of the school was expressed to the parents of another small boy in the words, "Send him to Chittenden's. It is the only place where I ever learnt anything." Mr. Chittenden, when asked who was the ablest pupil he had had, replied "Arthur Balfour," and, although this judgment was given after his quondam pupil had made a public reputation, no doubt he had been of the same opinion throughout. Mr. Chittenden was a man of wide general information, and an interesting talker, though a stern disciplinarian in school hours. Master and pupil seem to have had a warm regard for one another, and after the latter had left for Eton, it was Mr. Chittenden's favourite relaxation to visit him there. While at the school Mr. Chittenden often took him out for walks. An interest in music was one that they had in common, and it is probable too that they discussed scientific topics, with which Mr. Chittenden had some acquaintance. It is certain at least that Balfour dipped

* A fishing exploit at a very early age is remembered, however. He had succeeded in landing an eel, and was executing a dance in celebration of his victory with such vigour that he danced into a bed of stinging nettles. His yells of triumph soon gave place to yells attributable to a very different emotion.

into various branches of science at this time, though perhaps no more deeply than many boys do. The present writer possesses a copy of "Carpenter on the Microscope," with the inscription "A. J. Balfour, April, 1860, Eton College." Balfour is remembered to have brought home a frictional electrical machine, and to have made some attempts, though apparently without special tenacity or success, to carry out experiments in electrostatics, with home-made accessories.

As we have seen, he had impressed Mr. Chittenden, and at Eton he similarly impressed William Johnson,* who seems to have shown more discernment than most of Balfour's masters or contemporaries at this stage. His intellectual development was not precocious, but, in the event, it went on much longer than that of some of his early friends, who had, for a time, seemed to stand on a level with him. Indeed, it may be said that he went on developing almost to the end.

It has sometimes been thought that Balfour, like his uncle, Salisbury, found the atmosphere of Eton uncongenial. I am sure that he never said anything of the kind in my hearing: on the contrary he pressed strongly for some of his nephews to be sent there with the words "Much the best school." Nor was he disposed at all definitely to condemn the classical system of school education, though he was himself included in that large majority who, after spending years under the system, fail to acquire a working knowledge of the classical languages.

During the Lancashire cotton famine of 1862-63, Lady Blanche Balfour conceived the idea of saving money for the help of the distressed artisans, and incidentally providing a valuable practical experience for her young family by domestic economies. A projected trip to the continent was abandoned, and the household at Whittingehame was much reduced, the family helping with the housework. During the summer holidays Arthur Balfour and his brothers made the beds and blacked the boots, while his sisters did the cooking.

The time approached for him to go to the university. He had not made much progress in, or shown aptitude for mathematics, and it was necessary to make up for lost time. His sister, Eleanor (Mrs. Henry Sidgwick), remembers reading elementary trigonometry with him for the "Little-go." They had to make it out from a book as best they could without the help of a tutor, getting up early in the morning, and fortifying themselves with bread and milk for the effort. When they came to the point that $\sin \theta/\theta$ has the limiting value unity as θ is indefinitely diminished, Arthur Balfour was dissatisfied with the demonstration in the book (probably not without reason according to modern standards of mathematical rigour). But he thought the point would be interesting if one could fully understand it.

In later life he was deeply interested in the philosophical foundations of

* Later known as Cory.

mathematics, particularly in connection with the theory of probability, and deplored that he had not the technical knowledge to follow current developments either in that direction or in mathematical physics. He often regretfully commented "I expect it is too mathematical for me."

Within the family circle, he took his place as the leader in intellectual interests. He it was who usually discovered to the others new avenues in literature. For instance, he came back from school on one occasion brimming over with interest in "Goethe."

The social tact which distinguished him in later life was innate, and already apparent in his boyhood. He was somewhat careless in the matter of dress, and very much detached from the smaller anxieties of everyday life. For example, he was driving with his eldest sister to a dinner. She expressed doubts as to whether the coachman was going the right way. "That," said Balfour, "is his affair."

He went up to Trinity College, Cambridge, in the October term of 1866, as a fellow-commoner according to the custom of those days, as his father had done before him. This gave him the doubtful privilege of wearing a gown embroidered with silver,* and the valued one of sitting at the High Table with the dons. Here he was brought into contact with Henry Sidgwick and John Strutt (afterwards Lord Rayleigh) who were a few years senior to himself, and fellows of the college. With them he formed an enduring friendship, which in each case developed into something more. For the former eventually married his eldest sister, Eleanor (1876), and the latter his second sister, Evelyn (1871).

It does not appear that Arthur Balfour impressed his individuality very strongly on the High Table at Trinity. Rayleigh remembered a discussion there, a few years later, as to which of the Balfour brothers had the most ability. Some were for Gerald, others for Frank. When he himself put in a claim for Arthur, the general opinion seemed to be that he was propounding a paradox. There were no doubt substantial reasons for awarding the palm to his younger brothers at that time. They had achieved high academic success, whereas Arthur Balfour did not rise above the level of a second class in moral science. His tutor, Henry Sidgwick, who, with Rayleigh and Rayleigh's younger brother, Charles Strutt, had formed the highest opinion of him, was disappointed, but not altogether surprised by this result. Balfour was also somewhat disappointed himself, though academic success had not been a prominent aim in his mind. The explanation seems to have been that he had paid too much attention to the current problems of philosophy, and not enough to its literature and history.

The truth is that his was a mind which could ill submit to the bondage of following a prescribed course of study. With him the motive must be his

* He is said to have been the last, or almost the last fellow commoner.

own personal interest, not the fulfilment of a task. That was and remained repugnant to him whether an academic text book or the text of a parliamentary Bill was to be assimilated. In later life he several times gave public expression to his dislike of the tyranny of the examination system, though he did not pretend that it could be avoided.

Frank Balfour, who came up to Cambridge in 1870, took on the college rooms (A 4, New Court) which had been occupied by his elder brother, and was thus served by the same bedmaker. Adam Sidgwick, the zoologist, who was a devoted disciple of Frank Balfour, was fond of quoting her observation that "Mr. Arthur Balfour left a great many books about, but Mr. Frank read them through." Arthur Balfour had, in fact, an extraordinary faculty for getting hold of the essentials of a subject without apparently feeling the need for systematic study. Later in life when casually asked how long he could continue reading a stiff book, he put the limit, rather paradoxically perhaps, at ten minutes.

The following remarks* express his own point of view.

"We misuse the word superficiality, I think; sadly misuse it. Superficiality does not depend upon the amount of knowledge acquired. It is a quality rather of the learner than of the thing learned. The smallest amount of knowledge may be thorough in the sense in which the word should be used. Knowledge of the general principle may be obtained by those who have neither the time nor the ability to master the details of any particular branch of science; but to say that that smaller modicum of knowledge is therefore superficial, and therefore useless, is wholly to mistake what superficial knowledge consists in, and what education aims at. You may know very little, and not be superficial; you may know a great deal, and be thoroughly superficial. Superficiality is a quality of yourselves, not of the knowledge you acquire."

It was at about this stage of his career that he read Darwin's "*Origin of Species*," and its effect on his point of view was profound. His own mentality, it is true, was in many ways very different from that of Darwin. He had no store of detailed systematic knowledge, and it would probably not have been congenial to him to acquire it, or himself to attempt to sift the wheat from the chaff. But any one who reads the earlier chapters of the "*Foundations of Belief*" will see how much he had been influenced by the study of Darwin. Such reserve as he had was not founded on detailed criticism of Darwin's facts or methods of reasoning. The following quotation† will illustrate its nature.

"It is wrong to suppose that these supreme values [*i.e.*, what is highest and

* Speech at the opening of New Hall of Battersea Polytechnic, February 3, 1899 (*Times*). Reprinted in "*Arthur James Balfour as Philosopher and Thinker*," selection by Wm. Short 1912.

† '*Theism and Thought*,' p. 28.

rarest] in æsthetic ethics and thought seriously count in the struggle for existence. Saints, philosophers and artists have never, so far as I know, been specially successful in rearing large families themselves; nor have they enabled the communities which admired and occasionally produced them to crowd out rival populations from the rich places of the earth. As Nature measures utility, they are useless. In no effective fashion do they make for survival. They are but casual excrescences on the evolutionary process forming no part of its essential texture. They are, on the naturalistic hypothesis, an accident of an accident."

"Few things on the spiritual side of evolution are more interesting than this. It is not perhaps strange that the onward momentum of those developments which make for biological success should carry them into regions where all, or almost all, their survival efficiency vanishes away. But surely it is strange that they or something of them should acquire new and higher values which naturalism can hardly explain and certainly cannot justify."

Balfour throughout life had the highest admiration for Darwin, "because," he said "he was not a partizan—he really wanted to find out the truth—an attitude of mind seldom found among men of science, and never among theologians."

This opinion was not formed without the knowledge that comes of personal contact. He had been introduced to Darwin's home at Downe by the latter's son, George, who was one of his early friends at Cambridge, and to whom he remained warmly attached to the end.

Shortly after taking his degree, Balfour went with his friend, John Strutt, to visit the Gladstones at Hawarden Castle. Rayleigh often referred to an incident on this visit which evidently produced a strong impression upon him. For some reason it was necessary to ease the labours of the household, and in consequence Mr. Gladstone took Balfour and Strutt to dine at the village inn. Probably the two former took the chief part in conversation, and Strutt, it is likely, was a comparatively silent onlooker; be that as it may, he presently perceived that Balfour was not taking the veteran statesman seriously, but was amusing himself with a psychological study, and, as he often related the incident afterwards, "was playing Gladstone like a fish." Balfour's age at this time, be it remembered, was only twenty-two years.

The circumstances which led to Balfour's entering on a political career are explained in the fragment of autobiography, which will appear shortly. We are here rather concerned with the question of why he did not take up science. The following extract from his sister Evelyn, Lady Rayleigh's journal of September 10, 1888, will explain his own point of view:—

"Yesterday A. was as usual expressing a wish that he had been a scientific man instead of a politician."

E. "Why did you not devote yourself to science then?"

A. "I did not consider I was capable of it."

E. "John* does not agree with that, he says a conversation on science with you sometimes strains his powers."

A. "Oh, nonsense—but I was too lazy, I should never have had patience for the drudgery."

It is perhaps scarcely worth while to devote much consideration to what *might* have been. Other observers will probably agree with Balfour's own view that attention to drudgery was not his strong point. At the same time it is difficult to believe that he can have got through so many years of successful public life without having done a good deal of it.

He was certainly not an enthusiastic politician. He remarked on one occasion (1893) that his mind did not naturally run to politics. He never thought of them in bed, which was the test. He regarded them with a calm interest, but as for getting excited over them as some people did—he could not do it.

He was, I think, comparatively indifferent to both the trials and the rewards of official life as a party politician. He did not often trouble to inform himself as to what people were saying about him, and he seldom looked at a newspaper. He remarked that everything conceivable had been said of him, good, bad and indifferent, and that in view of this was difficult either to be much depressed or much elated by the sum total of the opinions expressed. He may have been somewhat hurt at having temporarily lost the confidence of the Unionist Party in 1911, but if this may be suspected it is not from anything that could be seen at the time, but from slight indications elicited by later events.

His detached attitude towards criticism may perhaps have made the sheltered life of a student relatively less attractive to him than to many others equally well qualified to pursue it. As to the honours and rewards of a public career, I know on the best authority possible that he accepted most of them with reluctance, and because circumstances made it difficult to do otherwise.

Finally, it may be remarked that most people realise more clearly the disadvantages of the career they have actually adopted than of the one they might have adopted and did not.

Balfour was first elected to Parliament as member for Hertford in 1874, and from this time on became increasingly immersed in public activities which do not fall within the scope of this notice; at no time, however, were his intellectual interests allowed to fall altogether into the background, and his first speculative work, "A Defence of Philosophic Doubt," appeared in 1879, shortly after his return from the Berlin Conference of 1878.

* Lord Rayleigh.

The title was not chosen without careful consideration, but none the less its meaning was widely misunderstood. As anyone who looks even casually into the book may see, doubt about the views of Mill and Spencer is advocated, not doubt about popular theology. "It appears," he says, "that the practical conclusions I draw from a sceptical philosophy have little or no tendency to alter the internal structure of any actual or possible creed."

The "Defence of Philosophic Doubt" discusses in turn each of the various theories of knowledge which at the time of writing could be considered to have any important following: J. S. Mill, Spencer, Kant, Hamilton, and the agnostic scientific school represented by writers like Huxley and Leslie Stephen, are each subjected in turn to a critical analysis, which is carefully limited to essentials. The author is never led into controversial bye-paths, however tempting, in order to score a point. He concludes that not one of these schools of thought is self-consistent, though he does not claim to be able to produce anything better. At the same time he carefully explains that he, like everyone else, cannot help accepting in practice the methods and conclusions of science, in spite of the incoherence he finds in them, regarded as a logical system. As a "practical result" he recommends that scientific conclusions should be provisionally adopted alongside of theological ones, even at the cost of apparent inconsistency. I do not know of any evidence that other thinkers at that time found themselves able specifically to accept this recommendation. It must be admitted, however, that an attitude very like this has been taken up in modern science, in using the wave theory of light to co-ordinate one set of phenomena, and the corpuscular theory to co-ordinate another set.

The general line of argument in this book has much in common with Balfour's second and better-known book, the "Foundations of Belief," on which he placed, perhaps, a higher value.

About the time of publication (December, 1894) he said, in intimate conversation, that he felt he had a message to give, which he was trying to give in this book, and which was of far greater importance than anything he had done or could do in politics. He was especially pleased and encouraged to find that his brother-in-law, Henry Sidgwick, though not always in agreement, thought highly of it; and as the public were anxious to have the views of a conspicuous public man on questions of such fundamental interest, the book sold largely.

In this, as in the author's other philosophical works, the greater part of the text is occupied with argument destructive of the philosophical point of view which he refers to as Naturalism, and, so far as I have been able to gather, it is this sceptical criticism, carried out with a wealth of illustration from the scientific field, and an easy dialectical mastery, which leaves the most marked impression on the minds of the generality of readers. As a brief example of the

method we may quote* "Though we are quite familiar with the fact that illusions are possible, and that mistakes will occur in the simplest observation, yet we can hardly avoid being struck by the incongruity of a scheme of belief whose premises are wholly derived from witnesses [the physiological mechanism of the senses] admittedly untrustworthy, yet which is unable to supply any criterion, other than the evidence of those witnesses themselves, by which the character of their evidence can in any given case be determined."

The author, however, was most anxious that the constructive part of his argument should not be overlooked, or misunderstood.

"I seem" he wrote† "to have given certain of my critics the impression that the principal, if not the sole object of this work, was to show that our beliefs concerning the material world and those concerning the spiritual world are equally poverty stricken in the matter of philosophic proof, equally embarrassed by philosophic difficulties. This, however, is not so . . . The dissipation of a prejudice, however fundamental, can at best be but an indirect contribution to the work of philosophic construction. Concede the full claims of the argument just referred to, yet it amounts to no more than this—that while it is irrational to adopt the procedure of naturalism, and elevate scientific methods and conclusions into the test of universal truth, it is *not* necessarily irrational for those who accept the general methods and conclusions of science to accept also ethical and theological beliefs which cannot be reached by these methods, and which, it may be, harmonise but imperfectly with these conclusions. This is indeed no unimportant result; yet, if the argument stopped here, it might not be untrue, though it would assuredly be misleading, to say that the following essay only contributed to belief in one department of thought by suggesting doubt in another. But the argument does not stop here. The most important part has still to be noted—that in which an endeavour is made to show that science, ethics, and (in its degree) aesthetics, are severally and collectively more intelligible, better fitted to form parts of a rational and coherent whole, when they are framed in a theological setting than when they are framed in one which is purely naturalistic."

During the interval between his retirement from the leadership of the Unionist Party in November, 1911, till the outbreak of war, Balfour had, perhaps, more leisure for intellectual pursuit than at any other period of his mature life, and a near observer described him as like a bird which had escaped from a cage. To this period belongs the photograph reproduced herewith,‡ the holiday attire in which he appears harmonising with his mood at the time. This interval of comparative leisure was partly employed in preparing the first series of Gifford lectures delivered at the University of Glasgow in

* "Foundations of Belief," 8th ed., p. 118.

† "Foundations of Belief." Introduction to 8th ed., pp. xvii, xviii, 1901.

‡ Taken by Admiral Strutt in the conservatory at Terling.

January and February, 1914, and published under the title "Theism and Humanism." The general scope and mode of treatment is not unlike that adopted in "The Foundations of Belief." Their success was extraordinary; the audiences amounted to something like two thousand and increased beyond the limit of seating accommodation as the course of ten lectures proceeded. He did his best to avoid technical language, which he considered was very apt to mask a confusion of thought; it was impossible however to avoid words like *empirical* and *a priori*. Two ladies were heard discussing who this *a priori* might be—some Italian philosopher they supposed. However, in spite of rather discouraging symptoms of this kind, he hoped and believed that most of his audience carried away something.

The services which Balfour's party had so easily dispensed with in times of peace were found necessary by his country in the hour of stress, and he was called to be First Lord of the Admiralty in May, 1915, shortly before the lectures were actually published. His brief interval of comparative leisure was at an end.

The second course of Gifford lectures was necessarily deferred till after the war. It was delivered in 1922-23 and published under the title "Theism and Thought."

Balfour, like many of his relatives, felt a sympathetic interest in psychical research. Some of his political followers were disposed to complain of this. They classed it with Bi-metallism and Female Suffrage, and considered that all these "fads" injured his position as a leader. When criticism of this kind came round to him, he said that he was not prepared to give up his "fads," and that if a choice was necessary he would sooner abandon politics.

In 1894 he gave a presidential address to the Society for Psychical Research.* In this, among other topics, he emphasised the warning to be taken from the incredulous attitude of the scientific world towards hypnotism. "There were, indeed, a good many doctors and other men of science who could not refuse the evidence of their senses, and who loudly testified to the truth, the interest, and the importance of the phenomena which they witnessed. But if you take the opinion of men of science generally, you will be driven to the conclusion that they either denied facts which were obviously true, or that they thrust them aside without condescending to submit them to serious investigation."

Balfour was, I believe, convinced of the reality of telepathy, and his conviction was fortified by some casual experiments with Prof. Gilbert Murray in which he took a personal part, and which excited a good deal of attention in the newspapers. On the alleged physical phenomena of spiritualism he had an open mind. He was, for example, unable lightly to dismiss the concurrent testimony of the late Lord Crawford and the late Lord Dunraven to some of the most marvellous happenings. He had known these men, and

* Reprinted in "Essays, Speculative and Political," 1920.

respected their capacity and good sense. Pressed to sum up, he answered, in a truly scientific spirit, that more experiments were needed.

As I have endeavoured to show, Balfour's knowledge of the essentials, rather than of the details of contemporary science, was wide. When he was called upon to speak publicly on scientific or semi-scientific questions he was usually able to illustrate a topic or to choose one from his own knowledge. Thus, when he was President of the British Association at Cambridge in 1904, he delivered an address in which what were then novel views of the electronic constitution of matter were discussed in their philosophical aspect. This was perhaps the first occasion when emphasis was laid before a popular audience on the glaring discrepancy between the new ideas of the atom, with its relatively vast inter-electronic spaces, and the old philosophic distinction which made shape a "primary" property of matter, existing independent of the observer, while secondary qualities, such as colour, were thought to have no such independence. It is not, I think, an exaggeration to say that these conceptions are found novel and illuminating by many educated people even now, more than a quarter of a century after the address was delivered.

Foreign savants who attended as guests of the Association were a good deal astonished at the range of scientific knowledge of the speaker, and some of them were disposed for a moment to doubt whether he could really be the Prime Minister, in part because he wore no decorations. After the opening meeting Balfour attended some of the sectional proceedings, in which he was able to take part. No doubt at times he used the arts of the experienced public man in making a necessarily limited knowledge go as far as possible. But he was always eager to learn more.

An incident remains in my mind as an illustration of this: it was, I think, during the autumn of 1928. We had been out for a country walk together, perhaps almost for the last time, and after the conversation had ranged over a great variety of topics including the morals of the present generation (which he did not think really worse than those which prevailed during his youth), the distribution of honours, the prospects of future taxation, and the literature of the eighteenth century, it came round, I do not remember exactly how, to the electromagnetic theory of light. "There are things I sometimes talk about," he said, "which I find it very difficult to get any grasp of. I think I understand pretty well the relations between electric currents and magnetism, but I cannot really form any conception of Maxwell's theory of the propagation of electromagnetic waves." I said I thought it was too difficult for general treatment. Maxwell's calculations must be followed through in order to get any insight into it.

He declined, however, to be put off in this way, and insisted on my trying to expound it. I did what I could, helping myself out with diagrams drawn on the road with a walking stick. However poor the attempt, he seemed fascinated

with the subject, and I remember trying to think of anyone else who would have been able to learn anything from such an explanation.

Relativity, occupying as it does the borderland between science and philosophy, interested him deeply. One remark he made on this subject is of some psychological interest, whether one is able to agree with it or not. He complained that the popular expositors put an undue and unnecessary stumbling block in the way of their readers when they traced out the paradoxical consequences of extreme suppositions, such as observers travelling on projectiles which moved with the velocity of light. I tried to plead that in science hard cases made good law, but he was not to be moved from his position. As regards the technique of physical measurements he was not so much interested. He could, of course, appreciate well enough the necessity of reaching a certain standard of precision in order to resolve a particular problem in hand; for instance, the standardisation of machine parts to go together without fitting. But he was not prepared to regard improved accuracy of measurement as an end in itself. This was evident enough to those who had the opportunity of discussing scientific subjects with him. Others will find an illustration of it in a reference to the measurement of solar parallax by the transit of Venus in one of his essays.*

Balfour was elected into the Royal Society under Statute 12 as early as 1888, and served on the Council in 1907-08 and again in 1912-14. In 1920 when the question of an election to the Presidency came up, the retiring President, Sir J. J. Thomson, was commissioned by the Council to find out whether Balfour would allow his name to be put forward, on the understanding that the Society would want him as an active, and not merely an ornamental president. Balfour was more than commonly pleased to receive so great a mark of the confidence of the scientific world; but he was already President of the British Academy; as Lord President he was responsible for the Department of Scientific and Industrial Research; he was taking a very leading part in the affairs of the League of Nations; and in addition to all this the Cabinet was meeting once, twice, or even three times a day. He felt that to add to this programme of work was impossible.

We have seen how Balfour had acquired a far wider scientific culture than usually falls to the lot of practical politicians. This culture had helped his philosophical studies, and had enabled him with the greater force to give public expression to his belief in the national importance of scientific pursuits. But otherwise it had not had much constructive outcome; nor can it have seemed likely in 1919 that at the age of 71 years it would ever do so. His political career seemed for the moment to be closing, and he was determined not to do any more heavy political work of the ordinary kind—leading the House of Lords, for example. He had always been inclined to rate rather low the value

* "Essays and Addresses," 3rd ed., 1905, pp. 23-24.

of what could be accomplished in that way* and he felt that he had earned his rest from it. Yet his public career was about to enter on a new phase, in which his scientific interests and acquirements were to bear no inconsiderable fruit. This phase seemed to himself more interesting and at least as important as any that had preceded it.

It is necessary to go back somewhat in time and to recall that in connection with Mr. Lloyd George's National Health Insurance Act of 1911, a large scheme of medical benefit was supplemented† by a considerable provision for medical research. Balfour spoke strongly in favour of this in the House of Commons, but the decision had apparently been taken already, and I have not been able to learn that he was definitely instrumental in bringing it about. The Medical Research Committee was the outcome in 1913, and this in 1919 became the Medical Research Council, under a Privy Council Committee and the Lord President. The war led to a great stimulus of State-supported science; for scientific problems arose in connection with almost every war activity. One may recall aeronautics, radio communications, anti-submarine work, poison gases, medical and surgical war problems such as antitetanus inoculation and plastic surgery, sound ranging—but the list is almost inexhaustible. In this way politicians and administrators were brought into contact with science and with scientific men. The ice was broken; budding scientific institutions underwent a forced growth; and when the war was over its lessons could not be unlearned, and the growth which had taken place proved on the whole to be permanent. It is a significant fact that when the post-war regime of retrenchment set in, it was not extended to research activities.

The Department of Scientific and Industrial Research was founded in 1915 and placed under the Lord President of the Council. Many new State scientific activities have been placed under the department—fuel research, low temperature research, building research, forest products research, chemical research, radio research, and two long-established scientific institutions, the Geological Survey and the National Physical Laboratory were also annexed to it.‡ The department has many other responsibilities besides these. It

* Extract from Lady Rayleigh's journal, June 16, 1892 :—" Paderewski was at the Royal Society Soirée last night, and in discussing it A. remarked of the scientific guests, ' They are the people who are changing the world and they don't know it. Politicians are but the fly on the wheel—the men of science are the motive power.' " The same point of view is more elaborately set out in his essay, " A Fragment on Progress," republished in " Essays and Addresses," 1905. See particularly pp. 260-262.

† Probably on the initiative of the late Sir Robert Morant, K.C.B., of the Education Office.

‡ The latter had been founded in 1900. Balfour was then First Lord of the Treasury, and was most sympathetic to the scheme. Indeed the suggestion that the laboratory should go to Bushy Park originated with him. War requirements had increased the extent of the laboratory's operations out of all knowledge, and it had become impracticable for the Royal Society to continue to carry the liability for balancing income and expenditure.

administers large funds for research purposes in academic institutions and industrial research associations.

Balfour, after his return from Paris in 1919, retired from the Foreign Office, in accordance with his determination to do no more heavy political routine, and undertook the lighter duties of Lord President. He then found himself in possession of the heritage which has just been sketched in outline. He probably had little up-to-date information about his new responsibilities, for since 1915 his time had been fully occupied at the Admiralty and the Foreign Office, and he cannot have been able to give much attention to anything else. One evening in the autumn of 1919 the Secretary of the Medical Research Council, who was somewhat pressed with work, was told that there was a gentleman to see him—Mr. Balfour. "I did not make any appointment, did I?" he said. "I do not think I can see him. What Mr. Balfour is it?" To his astonishment it turned out to be the Lord President. It was quite a new thing in his experience that a Minister should call on an official who served under him, and he had no reason to think that previous Lord Presidents had even known where the office was. Balfour opened the conversation by remarking that his new appointment seemed to give him very little to do, but that he was delighted to find that he was the head of two research organisations. He had come to learn whether there was anything he could do to help.

It soon appeared in practice that in those troublous times other ministerial duties and distractions made far greater claims than he had anticipated, and during the period of office from 1919 to 1922 when he went out at the fall of the Coalition Government, he was not able to attend the meetings of the Medical Research Council. As responsible minister he made no trouble about details. When formal matters were put before him he was content with the assurance of his advisers that all was right, and initialled them without further comment. "And now," he would say, "tell me something interesting."

For a short interval between 1922 and 1924 Balfour's connection with the Council was intermitted.

Lord Curzon became Lord President in 1924 and when Lord Irwin, who had been chairman of the Medical Research Council, went to India in 1925, Curzon sent to ask the advice of Balfour, who was not then in office, as to who should succeed him. It soon appeared that he was willing to serve himself, and so it was arranged. He became chairman, and attended every meeting. If he had a fault, it was not one that would be expected in a political chairman. He was if anything too prone to spend time at the council in discussing the scientific rather than the administrative aspects.

On Lord Curzon's death in 1925 Balfour again became Lord President, at Mr. Baldwin's special request. The problem then presented itself of whether

he could continue chairman of the advisory body, whose duty it was to give advice to himself.

The Council did not wish to lose him and arguments were readily found to justify the course which everybody desired should be taken. In the event he remained chairman until his last illness in 1930.

Balfour followed the developments of medical research with keen interest. He had known in his youth Sir James Simpson, of Edinburgh, the first to use chloroform as an anæsthetic, who was an intimate friend of Lady Blanche Balfour. He had early become acquainted with the methods of preventive inoculation by killed bacterial cultures by Sir Almroth Wright, to which he had become a firm convert. During the most active part of his Parliamentary career he was frequently placed *hors de combat* by feverish colds. It was often thought that these illnesses were merely diplomatic, but the suspicion was unfounded. He tried preventive inoculation, and benefited greatly from it. In this way he was brought into contact with the leading worker on the subject and his scientific interest was aroused. His friends and relatives heard a great deal at that time about streptococci and staphylococci. On the question of ordinary vaccination against smallpox his views were somewhat heterodox. In the autumn of 1898 he said in conversation with an intimate circle that he had been in favour of inserting a conscience clause into the Vaccination Act recently passed, and that since the Bill had passed he had looked somewhat further into the evidence, with the result that he had grave doubts whether vaccination was of any use at all. It was, he said, a question of statistics, not of science. In 1802, when vaccination was introduced, smallpox had decreased enormously, but much of the decrease had taken place, it was found, before vaccination became general. In 1876 when the belief in vaccination was at its height we had an epidemic of smallpox which threw into the shade the worst epidemics of the eighteenth century. There were, he said, other facts of a similar character.*

During Balfour's chairmanship of the Medical Research Council he did not fail to attend the occasional afternoon teas at the Council's Institute for Medical Research at Hampstead, when workers such as Gye and Barnard gave an account of the problems on which they were engaged. He took every opportunity of pointing out in occasional speeches the debt which the nation owes to medical research workers and the danger of allotting too large a share of the nation's gratitude and support to those who apply medical knowledge, to the neglect of those who originate it in the seclusion of the laboratory, far away from the public eye.

The Department of Scientific and Industrial Research benefited not less than the Medical Research Council from Balfour's connection with it, which

* These remarks are from a contemporary record. The present writer is not qualified to offer any comment upon them.

likewise began in the autumn of 1919. Here also he was in the habit of attending council meetings, sitting next to the chairman, Sir William McCormick, with whom he was on friendly terms. Indeed, friendliness was always the note in his relationship with civil servants, whether high or low. Thus, after official interviews at Balfour's house in Carlton Gardens, the secretary of the Department was commonly asked to stay to lunch, and the subject of discussion was often carried further in Balfour's family circle. The secretary's secretary was known to remark that during her official experience she had only twice been personally addressed by a Cabinet minister. The first time by one who shall be nameless, and who said "You may go"; the second time by Balfour, who said "Pray don't go, pray don't go."

To return however to the meetings of the advisory council. Balfour's contributions were mainly in the form of questions, which often opened a new point of view to the Council, and always referred to essentials.

His policy did not always err on the side of caution, and he was on occasion prepared to go beyond the advice of his Council. Thus the fuel research board which is under the department had been concerned with the hydrogenation of coal. There was the opportunity of purchasing for £35,000 ten years of experience on the problem, a half-scale plant, and all necessary opportunities for acquiring the knowledge to work it. The Council were not enthusiastic, some of them who were best qualified to express an opinion thought that the possibility of practical results was remote, and that the money from the limited budget would go further in other ways. However, a resolution of cold approval was eventually passed, and Balfour decided that the possibilities were so important from a national point of view that the expenditure was a legitimate gamble.

Again, when difficulty was anticipated in financing the promising work of the magnetic laboratory at Cambridge, under Dr. Kapitza, rather than that the work should be hindered, he was prepared to shoulder the responsibility of financing it from the department. This might be held to be somewhat irregular, but he expressed his willingness to defend it in Parliament. Had he been called upon to do so, his dialectical resources would, no doubt, have proved quite adequate to the occasion.

Balfour's attendance at the Council meetings, and his afternoon calls—unannounced and without appointment—at the secretary's office, were found most stimulating and encouraging. On the latter occasions, he would sit in an armchair discussing difficulties and hopes of achievement. He would ask what the truth really was about matters which were less ripe. Often the director of fuel research and other technical officers would be called in to the discussion, and the same sense of stimulus was experienced by them.

During Lord Curzon's term of office as Lord President, the question had

been mooted of devising machinery for co-ordinating the work of different government departments, and bringing the activities of the Research organisation now grouped under the Privy Council into more effective relation with them. The initiative came from members of the civil service. Lord Curzon's attitude was not very sympathetic at first, and further discussion was cut short by what proved to be his last illness. Balfour, as chairman of the Medical Research Council, was conversant, as Mr. Baldwin well knew, with these preliminary moves, and when he succeeded Curzon in office as Lord President (1925) Mr. Baldwin commissioned him specially to take up the problem.

One suggestion was to appoint a standing committee of leading scientific men. Balfour said "No. In the first place you are putting an undue burden on them. Secondly, you will have to make an invidious choice as to whom you ask to join the committee, and any man you select will be adapted perhaps to one problem, and not at all adapted to another. It would be far better to have a more elastic system and to imitate the organisation of the Committee of Imperial Defence."* Distinguished civil servants who had been called into consultation were soon won over to see the wisdom of this point of view.

The Committee of Imperial Defence, the reader may be reminded, was of Balfour's own contrivance. He devised it in 1904 when he was Prime Minister, because he found that no attempt was being made by the departments to pool their information, or to arrive at clear mutual understanding about war problems that might affect more than one of them. Thus the Navy said that *they* made us safe from invasion, while the Army said that we were in the greatest danger because *they* were not maintained at a sufficient strength; and the Post Office had no idea that *they* had anything special to do in war, though in fact the part they have to play is very important. And similarly in other cases.

The organisation originally set up by Balfour in 1904 to remedy this state of things is a committee, with only one permanent member—the Prime Minister. The other members are such persons as he may summon to sit—mainly his colleagues in the Cabinet, but also the heads of the fighting services, and occasionally other experts. But this is only the first stage. The detailed

* It is right to state that the idea of imitating Balfour's Committee of Imperial Defence for civil purposes was originally mooted by Lord Haldane as early as 1918.

The Labour Government of 1924, of which he was a member, considered the question further, apparently with economic rather than scientific enquiries in view; but nothing was done before they left office in the autumn of 1924. After the Labour Party returned to office in 1929, the organisation was modified in the way that Balfour had deprecated, and a standing committee was set up with the title of Economic Advisory Council. Whether this change will prove advantageous or permanent the future alone can show.

investigations are carried out by sub-committees in which a much larger latitude of choice is exercised, and there is as the backbone of the whole structure a permanent secretarial staff which serves the main committee and the sub-committees.

The above may seem somewhat of a digression, but its relevance will soon appear. Balfour's scheme of 1925 was closely copied from his scheme of 1904, and in fact it was possible to make use of the same offices and the same secretariat that already served the Cabinet and the Committee of Imperial Defence. Mr. Thomas Jones acted as principal secretary, with the assistance of Captain A. F. Hemming. The title chosen was the Committee of Civil Research.

Balfour was eager to make a beginning and to put the machinery thus created to the proof. The first subject of investigation was the Tsetse fly disease of Eastern and Central Africa. This had bearings both on health and on agriculture, and concerned the Colonial Office, the Fighting Services, the Foreign Office, and the Dominions. It was therefore typical of the kind of problem which the committee was created to deal with.

Balfour (acting for the Prime Minister) presided at the first meeting, and, as anticipated, a great lack of co-ordination was revealed. Under the Foreign Office many thousands a year were being spent in the Soudan, and spent to good advantage, particularly in the direction of quarantine. The Colonial Office representative admitted, under Balfour's cross-examination, that the Administration of Uganda knew nothing of this money being spent, and that they themselves had refused a trifling sum in respect of this kind of research. The man who was fighting the Tsetse fly in Uganda did not even know the man who was officially working at the same problem in the next colony.

The committee has remained active up to the time of writing. The Governor of Tanganyika who happened to be in England was later summoned to the committee, and as a result was glad to acknowledge the enlightenment it had given him, and to make consequent changes in his financial policy; and there were many other similar cases.

Balfour's influence did much to orient the policy of the Colonial Office towards the scientific aspect. This was the result of genuine conviction which he was able to impart, and not merely deference to superior authority. The machinery which he set up for the first time gave scientific men direct access to Ministers, without the intervention of lay officials, who were often unsympathetic to the scientific point of view, and deprived scientific advice of much of its effect.

Other scientific or semi-scientific subjects considered by the Committee of Civil Research during Balfour's regime (1925-29) were mineral content of natural pastures, Severn barrage, quinine supplies, dietetics, British pharmacopœia, research co-ordination, Kenya native welfare, geophysical surveying,

Great Barrier reef, mechanical transport, irrigation research, radium supplies, locust control.

The inauguration of the Committee of Civil Research was perhaps the last important achievement of Balfour's long career. The concluding phase of that career cannot be better summed up than in the words of one who was able to observe it at close quarters.*

"The Lord Presidency used to be considered a general utility office. He converted it into a Ministry of research. The idea was not born in his fertile brain, for a committee of the Privy Council for Scientific and Industrial Research and a similar committee for Medical Research, had been established during the war, and Lord Haldane's committee on the machinery of government had recommended the creation of such a Ministry. But Lord Balfour it was who turned an experiment, which many thought destined to disappear with other war-time devices, into a reality which is now generally recognised as a permanent and essential part of modern government. His unparalleled prestige in the political and intellectual worlds, his liberation from the rough-and-tumble of party politics were favourable circumstances, but his abiding faith in the power of science to promote the happiness and well-being of man, his enthusiastic interest in the advance of knowledge, his sympathy with the scientific outlook and with young people, and his long experience of the way in which things have to be done in Great Britain, were the decisive factors."

RAYLEIGH.

* Sir Frank Heath, G.B.E., K.C.B.

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